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Ab initio density functional theory (DFT) based on the optimized effective potential (OEP) method is a new approach to study the electronic structure of atomic, molecular and solid state systems. It contains elements of both wave function and density functional theories and is free from limitations of conventional DFT because of using orbital-dependent functionals derived from systematic approximations of the wave function theory.

Ab initio DFT methods with exchange-correlation functionals based on many-body perturbation theory (MBPT) have been derived and implemented recently. The exchange-correlation potentials derived from MBPT have a complicated structure and their derivation in higher-order of MBPT by the use of the chain-rule for functional differentiation requires significant effort. To facilitate such derivations, I developed a special diagrammatic formalism for taking functional derivatives. An alternative way to construct OEP MBPT exchange-correlation potentials is to use the density condition. It makes it possible to obtain potentials for different partitionings of the full molecular Hamiltonian with MBPT. Using the diagrammatic formalism developed for taking functional derivatives, we show an order-by-order equivalence between the functional derivative and the density condition approaches to OEP MBPT for the case of the Kohn-Sham partitioning of the molecular Hamiltonian. For any other partitionings, different
exchange-correlation potentials are produced by the functional derivative and density condition approaches.

The time-dependent extension of OEP in the adiabatic approximation with exchange-only potentials and kernels was recently implemented and applied to some molecular systems. The corresponding excitation energies and polarizabilities are in good agreement with time-dependent Hartree-Fock results. However, such results cannot be used for comparison with experimental values due to lack of a description of electron correlation effects. In order to account for correlation effects, a correlation kernel corresponding to the MBPT(2) potentials has been derived. Its structure and properties are described in detail. The first numerical results for excitation energies with pure ab initio potentials and kernels are presented.

The recently implemented OEP MBPT(2) method has been extended to the case of spin-polarized open-shell systems. The total energies obtained for several open-shell systems are very close to the corresponding values obtained with the highly-correlated coupled cluster singles and doubles with perturbative triples (CCSD(T)) method. Comparison with results obtained with the OEP MBPT(2) exchange-correlation potentials and some density functionals has shown a qualitatively incorrect shape for some widely used exchange-correlation potentials.

Higher-order response properties, such as hyperpolarizabilities, are described very poorly with conventional functionals. The typical relative errors described in the literature are about 100 percent. The reason for the poor description is an incorrect long-range asymptotic behavior and an incomplete cancellation of the coulombic self-interaction. The OEP method is free from those drawbacks and calculated values of static hyperpolarizabilities with the exchange-only potential are close to those derived from Hartree-Fock theory. The second kernel required for calculations of hyperpolarizabilities within the DFT framework has been derived for OEP potentials by using the developed
diagrammatic technique. The structure and properties of the second OEP kernel are discussed.
CHAPTER 1
INTRODUCTION

The definition of a chemical reaction as a transformation of one substance to another at the molecular level means a regrouping of nuclei and electrons. In the adiabatic approximation, such nuclear regroupings can be presented as a motion in the field of some potential, also known as a potential energy surface. Potential energy surfaces can be obtained by solving the eigenvalue problem with the so called electronic Hamiltonian

\[ \hat{H}_{el} = -\frac{1}{2} \sum_{i=1}^{\text{elec}} \nabla_i^2 - \sum_{i=1}^{\text{elec}} \sum_{A=1}^{\text{Nucl}} \frac{Z_A}{|r_i - R_A|} + \sum_{i<j}^{\text{elec}} \frac{1}{|r_i - r_j|} \]  

(1-1)

Whole nuclear coordinates are treated as a set of parameters. If there are more than two particles in the system, the eigenvalue problem

\[ \hat{H}_{el}(R_1...R_M)\Psi(r_1...r_N, R_1...R_M) = E(R_1...R_M)\Psi(r_1...r_N, R_1...R_M) \]  

(1-2)

can not be solved analytically. For the calculation of electronic energy levels, some approximations have to be used.

Modern quantum chemistry includes three classes of methods for the solution of the electronic problem. The first one, called wave function theory, uses different approximations for the calculation of the wave function \( \Psi(r_1...r_N, R_1...R_M) \) and the corresponding energy \( E(R_1...R_M) \). The second class, known as density functional theory uses the density as a primary object. Within the DFT approach, the energy is written as a functional of density, and the construction of the wave functions is not necessary. The third class of methods uses a whole density matrix. The density matrix renormalization group (DMRG) and the density matrix functional theory (DMFT) are typical methods of the third class.

Ab initio DFT contains elements of the first two classes. It uses a local multiplicative potential, typical for the DFT approach. However, the corresponding exchange-correlation
potentials are derived from orbital-dependent energy functionals, taken from wave function theory.

The main advantage of wave-function based methods is the possibility to obtain systematically improvable results. This means that with the extension of the basis set, it will be possible to obtain more accurate energies and wave functions, and in the complete set it is possible to get the exact solution of the Schrödinger equation. On the other hand, rigorous \textit{ab initio} methods using wave function methods are usually very costly for computations on large molecules. Ab initio wave function methods can usually be applied only for systems with \(\sim 20\text{-}30\) atoms in reasonable basis sets. The main DFT advantage is a small computational cost; it can handle systems with several hundreds of atoms. However, most of conventional density functionals do not have the capacity to produce systematically improvable results.

Ab initio DFT is capable of producing systematically improvable results, but it is computationally more costly than DFT with conventional functionals. Despite its computational cost, ab initio DFT can be used as a method for the calibration of density-dependent functionals. An alternative way of providing such information is Quantum Monte-Carlo (QMC) method, however, QMC results are not available for molecules and open-shell systems.

1.1 Ab Initio Wavefunction-Based Methods

1.1.1 Hartree-Fock Method

In the Hartree-Fock method, a wave function is considered as a \textit{Slater determinant}[1]

\[
\Psi_{HF} = \begin{vmatrix}
\psi_1(r_1) & \cdots & \psi_1(r_N) \\
\vdots & \ddots & \vdots \\
\psi_N(r_1) & \cdots & \psi_N(r_N)
\end{vmatrix}
\]

The single-electron wave functions \(\psi_i(r)\) (or \textit{orbitals}) are determined by the condition that the corresponding determinant minimizes the expectation value of the electronic
Hamiltonian

\[ E_{HF} = \text{min} \ < \Psi_{HF} | \hat{H} | \Psi_{HF} > \]  

subject to the condition of orthonormality on the orbitals \(< \varphi_i | \varphi_j > = \delta_{ij}\). Substituting

the explicit form of the wave function from Equation (1–3) into an expectation value, it is

possible to write the Hartree-Fock energy in terms of orbitals

\[ E_{HF} = \sum_{i}^{\text{elec}} < \varphi_i | -\frac{1}{2} \nabla^2 - \sum_{A}^{\text{Nuc}} Z_A | r_i - R_A | | \varphi_i > + \frac{1}{2} \sum_{i,j}^{\text{elec}} (< \varphi_i \varphi_j | \varphi_i \varphi_j > - < \varphi_i | \varphi_j | \varphi_j | \varphi_i >) \]  

(1–5)

To derive the Hartree-Fock equations it is convenient to minimize the following

functional

\[ I = E_{HF} - \sum_{i,j}^{\text{elec}} \varepsilon_{ij} < \varphi_i | \varphi_j > \]  

(1–6)

where \(\varepsilon_{ij}\) - are Lagrange multipliers. Minimization of the functional from Equation (1–6)

requires that the functional derivatives of \(I\) with respect to the orbitals vanish

\[ \frac{\delta I}{\delta \varphi_i} = 0, \frac{\delta I}{\delta \varphi_i^*} = 0 \]  

(1–7)

Taking into account Equation (1–3) condition (1–7) can be presented as

\[ f \varphi_i = \sum_{j} \varepsilon_{ij} \varphi_j \]  

(1–8)

The operator \(f\) has the structure

\[ f = -\frac{1}{2} \nabla^2 + \hat{v}_{\text{ext}} + \hat{v}_H + \hat{v}_{\text{nlx}} \]  

(1–9)
where

\[ \hat{v}_{\text{ext}}(r) = -\sum_{i}^{\text{elec}} \sum_{A}^{\text{Nucl}} \frac{Z_{A}}{|r_{i} - R_{A}|} \]

\[ \hat{v}_{H}(r) = \sum_{j} \int \frac{\varphi_{j}^{*}(r_{1})\varphi_{j}(r_{1})}{|r - r_{1}|} dr_{1} = \int \frac{\rho(r_{1})}{|r - r_{1}|} dr_{1} \]

\[ \rho(r) = \sum_{j}^{\text{elec}} \varphi_{j}^{*}(r)\varphi_{j}(r) \quad (1-10) \]

The Hartree-Fock exchange operator \( \hat{v}_{\text{nlx}} \) is non-local, i.e. it cannot be presented as an analytical function of spatial variables. However, it is possible to write its action on some orbital \( \varphi_{i} \)

\[ \hat{v}_{\text{nlx}}\varphi_{i}(r) = \sum_{j} \int \frac{\varphi_{j}^{*}(r_{1})\varphi_{i}(r_{1})}{|r - r_{1}|} \varphi_{j}(r) dr_{1} \quad (1-11) \]

Since the Fock operator \( \hat{f} \) is hermitian and \( v_{H}(r) \) and \( \hat{v}_{\text{nlx}}\varphi_{i}(r) \) are invariant with respect to unitary transformations of orbitals, Equation (1-8) can be rewritten in the canonical form

\[ \hat{f}\varphi_{i} = \varepsilon_{i}\varphi_{i} \quad (1-12) \]

This form of the Hartree-Fock method is most common for practical implementations.

The Hartree-Fock method is a system of integro-differential equations, which cannot be solved analytically. Iterative methods can be used for the approximate solution of the Hartree-Fock equations with a given accuracy. As a first step some guess of orbitals should be assumed and substituted into the equations. During the second step the system of equations is solved and a new guess for the orbitals is obtained. Then those new orbitals should be substituted into the equations again, until the total energy and density at successive iterations differs less than a required accuracy. This is known as the self-consistent field (SCF) method.

For practical purposes molecular orbitals are usually presented as being decomposed into Gaussian functions, centered on the nuclei. In this case the number of solutions is much larger than the number of electrons. To decide which orbitals should be included
into the Slater determinant, the Aufbau principle should be used. Consider the increasing orbital energies in the order

\[ \varepsilon_1 < \varepsilon_2 < \varepsilon_3 \ldots < \varepsilon_N \ldots < \varepsilon_M \]  

(1–13)

where \( N \) - number of electrons and \( M \) - number of solutions. According to the Aufbau principle, the corresponding first \( N \) spin-orbitals should constitute the Slater determinant. Such orbitals are called occupied orbitals and the rest of the orbitals called virtual orbitals.

### 1.1.2 Electron-Correlation Methods

The Hartree-Fock method can recover up to 99% of the total electronic energy. Yet, even the remaining error of 1% is too big from the point of view of chemistry and can lead to qualitatively wrong predictions of electronic structure.

The difference between the Hartree-Fock and the exact solution is due to electron-correlation effects. The primary concern of electron-correlation methods is to develop many-body techniques for going beyond the Hartree-Fock approximation and taking into account the simultaneous electron-electron interactions. These methods, contrary to the relatively simple Hartree-Fock approximation, can be quite challenging conceptually and costly, computationally.

The correlation limit can be obtained from the Full Configuration Interaction (FCI) method. In this approach the total electronic wave function is expressed in the following way

\[
\Psi_{\text{FCI}} = \Phi_{\text{HF}} + \sum_{i}^{\text{occ}} \sum_{a}^{\text{virt}} C_i^a \Phi_i^a + \sum_{i \neq j}^{\text{occ}} \sum_{a \neq b}^{\text{virt}} C_{ij}^{ab} \Phi_{ij}^{ab} + \ldots
\]  

(1–14)

where \( \Phi_i^a, \Phi_{ij}^{ab}, \ldots \) are Slater determinants, formed by substitution of occupied orbitals \( i, j \ldots \) by virtual orbitals \( a, b \ldots \) with the corresponding reordering of rows. The expansion coefficients are found from the variational condition on the expectation value of the Hamiltonian

\[
E_{\text{FCI}} = \min_{C_i^a, C_{ij}^{ab}, \ldots} \frac{\langle \Psi_{\text{FCI}} | \hat{H} | \Psi_{\text{FCI}} \rangle}{\langle \Psi_{\text{FCI}} | \Psi_{\text{FCI}} \rangle}
\]  

(1–15)
However, the number of possible excited determinants grows rapidly with the number of electrons and basis functions in the system. Therefore, the full CI method is computationally intractable for any but very small systems. Among the approximate electron-correlation approaches, the most common are the Coupled Cluster method[2] and Many - Body Perturbation Theory[3]. Any truncated version of the CI method has a qualitatively wrong behavior of the energies and wave functions while increasing the number of particles in the system. Therefore, the CI methods with limited level of excitations cannot be used for highly-correlated systems. The Coupled Cluster method and Many - Body Perturbation theories are free from this lack of extensivity failure and are very common for the molecular computations. In some cases perturbation theory can provide an accurate description of electron-correlation effects at a much lower cost than necessary for the Coupled Cluster method. The second-order Rayleigh-Schrödinger perturbation theory is the simplest and least expensive ab initio method for taking into account electron correlation effects.

In this perturbation theory the solution of Schrödinger equation

$$\hat{H}\Psi = E\Psi$$  (1–16)

can be found using the Slater determinant as a reference. Generally, such a determinant may be constructed from the orbitals, generated by some one-electron operator

$$\hat{h}\varphi_p = (-\frac{1}{2}\nabla^2 + \hat{u})\varphi_p = \varepsilon_p\varphi_p$$  (1–17)

The first step of any perturbation theory is the partitioning of the Hamiltonian into a zero-order $H_0$ and perturbation

$$\hat{H} = \hat{H}_0 + \hat{V}$$  (1–18)

where

$$\hat{H}_0\Phi = E_0\Phi = \sum_i (h_i)\Phi = (\sum_i \varepsilon_i)\Phi$$  (1–19)
The perturbation operator is usually defined as the difference between the full and the zero-order Hamiltonians

\[ \hat{V} = \hat{H} - \hat{H}_0 = \sum_i \hat{v}_{\text{ext}}(r_i) - \sum_i \hat{u}(r_i) + \sum_{i \neq j} \frac{1}{|r_i - r_j|} \]  

Introducing \( \lambda \) as the small perturbation parameter, the Hamiltonian and the wave function can be written as

\[ \hat{H} = \hat{H}_0 + \lambda \hat{V} \]  
\[ \Psi = \Phi + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \ldots \]  
\[ E = E_0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \]

These order-by-order corrections can be found by substituting expansions (1–21), (1–22) and (1–23) into (1–16) and collecting terms with the corresponding order in \( \lambda \)

\[ (E_0 - \hat{H}_0)|\Psi^{(1)}> = (\hat{V} - E^{(1)})|\Phi> \]  
\[ (E_0 - \hat{H}_0)|\Psi^{(2)}> = (\hat{V} - E^{(1)})|\Psi^{(1)}> - E^{(2)}|\Phi> \]

Choosing the perturbative corrections to be orthogonal to the reference determinant \( <\Psi^{(n)}|\Phi> = 0 \) (so called intermediate normalization) it is easy to get the expressions for perturbative corrections at any order. Projecting the equations (1–24) and (1–25) onto the reference determinant expressions for energy corrections are obtained

\[ E^{(1)} = <\Phi|\hat{V}|\Phi> \]  
\[ E^{(2)} = <\Phi|\hat{V}|\Psi^{(1)}> \]

Expressions for the order-by-order expansion of wave functions can be written using the resolvent operator\[4\]

\[ |\Psi^{(1)}> = \hat{R}_0 \hat{V} |\Phi> \]  
\[ |\Psi^{(2)}> = \hat{R}_0 (\hat{V} - E^{(1)}) |\Psi^{(1)}> = \hat{R}_0 (\hat{V} - E^{(1)}) \hat{R}_0 \hat{V} |\Phi> \]
where
\[
\hat{R}_0 = \frac{\hat{Q}}{E_0 - \hat{H}_0}
\]
and \(\hat{Q} = 1 - |\Phi > < \Phi|\) is the projector onto the complementary space of \(|\Phi >\). Since \(\hat{H}_0\) is diagonal in the basis of Slater determinants, it is possible to write
\[
\hat{R}_0 = \sum_{n \neq 0} \frac{|\Phi_n > < \Phi_n|}{E_0 - E_n}
\]

For the special case of the Hartree-Fock reference determinant
\[
E_0 + E^{(1)} = < \Phi | \hat{H}_0 | \Phi > + < \Phi | \hat{V} | \Phi > = E_{HF}
\]
the second-order correction to the energy is
\[
E^{(2)} = \frac{1}{2} \sum_{i,j}^{occ} \sum_{a,b}^{unocc} \frac{< ij | ab > ( < ij | ab > - < ij | ba >)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}
\]
For the case of a more general reference determinant, constructed from orbitals of Equation (1–17), the second-order correction to the energy has the following structure
\[
E^{(2)} = \sum_{i}^{occ} \sum_{a}^{unocc} \frac{| < i | \hat{h} - \hat{f} | a > |^2}{\varepsilon_i - \varepsilon_a} + \frac{1}{2} \sum_{i,j}^{occ} \sum_{a,b}^{unocc} \frac{< ij | ab > ( < ij | ab > - < ij | ba >)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}
\]

1.2 Kohn-Sham Density Functional Theory

Density Functional Theory is an alternative approach to the description of the electronic structure of molecular and solid-state systems. This method uses electronic density instead of the wave function as the basic object of theory. The mathematical basis of DFT is provided by two theorems, introduced by Kohn, Hohenberg and Sham. The first one, known as Hohenberg-Kohn theorem\[5\], establishes a one-to-one mapping between the ground-state electronic density and the external potential. The external potential defines a particular object (atom, molecule, etc) and, because of the one-to-one mapping, the density contains all the information about the system. In particular, the ground-state energy can be written as a functional of the density. To get the ground state energy in
terms of the density, the Kohn-Sham theorem[6] can be used. This theorem states, that the ground-state energy as a functional of density has a minimum, if the density is exact. Therefore, given the energy functional, one can obtain the ground-state density and energy by variational minimization of the functional. The formal definition of DFT does not tell how to construct such a functional. Several approximate forms have been suggested, however, whose accuracy varies greatly for different properties. The kinetic energy of electronic motion is particularly difficult to approximate as a density functional.

The basic idea of Kohn and Sham was to transform the variational search over the density into a search over the orbitals that integrate to a given trial density

$$(-\frac{1}{2}\nabla^2 + v_s(r))\varphi_p(r) = \varepsilon_p\varphi_p(r) \quad (1-35)$$

Such a transformation does not restrict the variational space, provided that every physically meaningful density corresponds to a unique set of orbitals (the \(v\)-representability condition). The use of the Kohn-Sham SCF model ensures not only that the variational density is a fermionic density, but it also provides a good approximation for the kinetic energy. If orbitals integrate to the true density it is natural to expect that

$$T_s = -\frac{1}{2} \sum_i^{\text{elec}} <\varphi_i|\nabla^2|\varphi_i> \quad (1-36)$$

accounts for a large part of real kinetic energy.

The rest of the unknown terms are grouped into the exchange-correlation functional

$$E_{xc}[\rho] = E[\rho] - T_s - E_{ext} - E_H \quad (1-37)$$

where \(E_H\) is a Hartree energy and can be easily be calculated from a given set of Kohn-Sham orbitals. The non-interacting kinetic energy \(T_s\) is supposed to reproduce a large part of the exact kinetic energy \(T\). Therefore, \(E_{xc}\) is easier to approximate as a density functional than the total energy \(E\).
The definition of the exchange part of $E_{xc}$ can take into account its definition in wave-function theory,

$$E_x = \langle \Phi_s | V | \Phi_s \rangle - E_H$$  \hspace{1cm} (1–38)

Kohn-Sham orbitals are defined by an effective local potential $v_s$. Transforming the variational condition on the energy functional into a condition for the constrained search over the orbitals, it is possible to write

$$v_s(r) = \frac{\delta(E[\rho] - T_s)}{\delta \rho} = \frac{\delta(E_{ext} + E_H + E_{xc})}{\delta \rho} = v_{ext} + v_H + v_{xc}$$ \hspace{1cm} (1–39)

where the exchange-correlation potential is defined as the functional derivative of the exchange-correlation energy

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)}$$ \hspace{1cm} (1–40)

Once $E_{xc}$ is approximated and the Kohn-Sham equations are solved, the total energy can be found from the following expression

$$E = \sum_{i=1}^{\infty} \varepsilon_i - \frac{1}{2} \int dr_1 dr_2 \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} - \int dr_1 \rho(r_1) v_{xc}(r_1) + E_{xc}$$ \hspace{1cm} (1–41)

The solution of the Kohn-Sham equations is completely analogous to the solution for the Hartree-Fock case, and it is usually done by an SCF procedure. After self-consistency is reached, the Kohn-Sham orbitals are guaranteed to reproduce the true density of the many-electron system.

Virtually all modern implementations of DFT use the Kohn-Sham scheme. However, the theory still has open questions as to how to construct the exchange-correlation functional. Thus, the main challenge for the theoretical development of DFT remains the construction of accurate exchange-correlation functionals.

1.2.1 Time-Dependent Density Functional Theory

The Kohn-Shame scheme provides the possibility to describe ground state energies and densities. For the description of excitation energies a time-dependent generalization of conventional DFT can be used. Ordinary time-dependent DFT is based on the existence
of an exact mapping between densities and external potentials. In the ground state formalism, the existence proof relies on the Rayleigh-Ritz minimum principle for the energy. A straightforward extension to the time-dependent domain is not possible since a minimum principle is not available in this case. The existence proof for the one-to-one mapping between time-dependent potentials and time-dependent densities, was first given by Runge and Gross[7].

We can start from the time-dependent Schrödinger equation

$$i \frac{\partial \Psi(t)}{\partial t} = \hat{H}(t)\Psi(t)$$ \hspace{1cm} (1–42)

evolving from a fixed initial many-particle state

$$\Psi(t_0) = \Psi_0$$ \hspace{1cm} (1–43)

under the influence of different external potentials \(v(r,t)\). For each fixed initial state \(\Psi_0\), the formal solution of the Schrödinger equation (1–42) defines a map

$$A : v(r,t) \mapsto \Psi(t)$$ \hspace{1cm} (1–44)

between the external potential and the corresponding time-dependent many-particle wave function and a second map

$$B : \Psi(t) \mapsto \rho(r,t) = < \Psi(t)|\hat{\rho}(r,t)|\Psi(t) >$$ \hspace{1cm} (1–45)

Thus, the following mapping can be established:

$$G : v(r,t) \mapsto \rho(r,t)$$ \hspace{1cm} (1–46)

The Runge-Gross theorem establishes that the \(G\) mapping is invertible up to some additive, time-dependent constant. In other words, two densities \(\rho(r,t)\) and \(\rho'(r,t)\) evolving from the common ground state \(\Psi_0\) under the influence of potentials \(v(r,t)\) and
$v'(r,t)$ are always different, if

$$v(r,t) \neq v'(r,t) + C(t)$$ (1–47)

After invertibility for the G mapping is established, the action functional can be introduced

$$A[\rho] = \int_{t_0}^{t_1} dt < \Psi[\rho](t)|i \frac{\partial}{\partial t} - \hat{H}|\Psi[\rho](t)>$$ (1–48)

and the variational condition can be applied,

$$\frac{\delta A[\rho]}{\delta \rho(r,t)} = 0$$ (1–49)

Using the same manipulations as for the ground state a set of one-particle equations can be derived

$$i \frac{\partial}{\partial t} \varphi_i(r,t) = \left( -\frac{1}{2} \nabla^2 + v_s[\rho(r,t)] \right) \varphi_i(r,t)$$ (1–50)

where

$$v_s[\rho(r,t)] = v_{ext}(r,t) + \int dr' \rho(r',t) + v_{xc}[\rho](r,t)$$ (1–51)

The great advantage of the time-dependent Kohn-Sham scheme lies in its computational simplicity compared to other electron-correlation methods. The time-dependent Kohn-Sham scheme with explicit time-dependence of the density and the potential can be applied for any type of external, time-dependent potentials. However, when the time-dependent external potential is small it can be treated with time-dependent perturbation theory. If the applied perturbation is a periodic electromagnetic field, it is more convenient to use response theory.

### 1.2.2 Time-Dependent Density Functional Theory Linear Response Theory

Consider the N-electron system being initially, i.e. at $t < t_0$ in its ground state. In this case the initial density $\rho_0$ can be calculated from the ordinary ground-state Kohn-Sham equation

$$\left( -\frac{1}{2} \nabla^2 + v_0(r) + \int dr' \frac{\rho_0(r')}{|r - r'|} + v_{xc}[\rho_0](r) \right) \varphi_i^{(0)}(r) = \varepsilon_i^{(0)} \varphi_i^{(0)}(r)$$ (1–52)
At \( t = t_0 \) the perturbation is applied so that the total potential is given by

\[
v(r, t) = v_0(r) + v_1(r, t)
\]  

(1–53)

where \( v_1(r, t) = 0 \) for \( t \leq t_0 \).

The objective is to calculate the linear density response \( \rho_1(r, t) \) to the perturbation \( v_1(r, t) \). Conventionally, \( \rho_1(r, t) \) is computed from the full linear response function \( \chi \) as

\[
\rho_1(r, t) = \int dr \int_{t_0}^{\infty} dt' \chi(r, t, r', t') v_1(r', t')
\]  

(1–54)

Since the time-dependent Kohn-Sham equations (1–50) provide a formally exact way of calculating the time-dependent density, it is possible to compute exact density response \( \rho_1(r, t) \) as the response of the non-interacting system

\[
\rho_1(r, t) = \int dr' \int_{t_0}^{\infty} dt' \chi_{KS}(r, t, r', t') v_1^{(1)}(r', t')
\]  

(1–55)

where \( v_1^{(1)}(r, t) \) is the effective time-dependent potential evaluated to first order in the perturbing potential, i.e.,

\[
v_1^{(1)}(r, t) = v_1(r, t) + \int dr' \frac{\rho_1(r', t')}{|r - r'|} + \int dr' \int dt' f_{xc}(r, t, r', t') \rho_1(r', t')
\]  

(1–56)

The exchange-correlation kernel \( f_{xc} \) is given by the functional derivative of \( v_{xc} \)

\[
f_{xc}(r, t, r', t') = \frac{\delta v_{xc}[\rho](r, t)}{\delta \rho(r', t')}
\]  

(1–57)

at \( \rho = \rho_0 \).

While the full response function \( \chi \) is very hard to calculate, the non-interacting \( \chi_{KS} \) can be computed fairly easily. In terms of the static Kohn-Sham orbitals the Fourier transform of \( \chi_{KS}(r, t, r', t') \) with respect to \( (t - t') \) can be expressed as

\[
\chi_{KS}(r, r', \omega) = \lim_{\delta \to 0^+} \sum_{i}^{\text{occ}} \sum_{a}^{\text{unocc}} \frac{\phi_i(r) \phi_a(r) \phi_i(r') \phi_a(r')}{\omega - (\epsilon_i - \epsilon_a)}
\]  

(1–58)
Equations (1–55) and (1–56) are the basis of linear response theory. Since equation (1–55) is not linear with respect to $\rho_1$ the solution should be obtained by some iterative procedure.

However, for all practical purposes a direct use of equation (1–55) is not convenient. To get a more convenient form, the following matrix element should be considered

$$< \varphi_a | \rho_1(\omega) | \varphi_i > = < \varphi_a | v_1(\omega) | \varphi_i > + \int dr \varphi_a(r) \left( \int dr' \frac{\rho_1(r', \omega)}{|r - r'|} \right) \varphi_i(r) + \int dr \varphi_a(r) \left( \int dr' f_{xc}(r, r', \omega) \rho_1(r', \omega) \right) \varphi_i(r) \quad (1–59)$$

On the other hand, $< \varphi_a | \rho_1(r, \omega) | \varphi_i >$ can be expressed in terms of a response function

$$\rho_1(r, \omega) = \sum_{i} \sum_{a} P_{ia}(\omega) \varphi_a \varphi_i + P_{ai}(\omega) \varphi_a \varphi_i \quad (1–60)$$

where

$$P_{ia}(\omega) = - < \varphi_i | v_1(\omega) | \varphi_a > \frac{1}{\omega + (\varepsilon_a - \varepsilon_i)} , P_{ai}(\omega) = - < \varphi_i | v_1(\omega) | \varphi_a > \frac{1}{(\varepsilon_a - \varepsilon_i) - \omega} \quad (1–61)$$

Substituting equation (1–61) into equation (1–59) we have

$$- P_{ia}(\omega) (\omega + \varepsilon_a - \varepsilon_i) = < \varphi_a | v_1(\omega) | \varphi_i > + \sum_{j} \sum_{b} \left( < \varphi_i | \varphi_j | \varphi_a \varphi_b > + < \varphi_i | f_{xc}(\omega) | \varphi_a \varphi_j > P_{jb} + < \varphi_i | \varphi_b | \varphi_a \varphi_j > P_{ij} \right)$$

$$- P_{ai}(\omega) (\varepsilon_a - \varepsilon_i - \omega) = < \varphi_i | v_1(\omega) | \varphi_a > + \sum_{j} \sum_{b} \left( < \varphi_i | \varphi_b | \varphi_a \varphi_j > + < \varphi_i | f_{xc}(\omega) | \varphi_a \varphi_j > P_{jb} + < \varphi_a | \varphi_b | \varphi_i \varphi_j > + < \varphi_a | f_{xc}(\omega) | \varphi_i \varphi_j > P_{ij} \right) \quad (1–62)$$

Introducing the notations

$$A_{ai, bj} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + < \varphi_i \varphi_j | \varphi_a \varphi_b > + < \varphi_i \varphi_j | f_{xc}(\omega) | \varphi_a \varphi_b >$$

$$B_{ai, bj} = < \varphi_i \varphi_b | \varphi_a \varphi_j > + < \varphi_i \varphi_b | f_{xc}(\omega) | \varphi_a \varphi_j > \quad (1–63)$$
equation (1–62) can be rewritten in the following matrix form

\[
\begin{pmatrix}
A & B \\
B & A
\end{pmatrix} + \omega
\begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
P \\
P^+
\end{pmatrix} =
\begin{pmatrix}
v_1(\omega) \\
v_1^+(\omega)
\end{pmatrix}
\]

This equation provides a possibility to calculate the linear response of the density, caused by the external perturbation \(v_1(r, \omega)\). If the frequency of the applied electromagnetic field is equal to some resonance frequency (i.e. frequency, which correspond to a transition to some excited state) even an infinitesimal perturbation causes a finite response of the density. In this case equation (1–64) can be rewritten as [8–11]

\[
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
P \\
P^+
\end{pmatrix} = \omega
\begin{pmatrix}
P \\
P^+
\end{pmatrix}
\]

Equation (1–65) is common for the calculation of excitation energies with time-dependent density functional theory (TDDFT). Most modern implementations of TDDFT use the frequency-independent exchange-correlation kernels, defined as a simple functional derivative

\[
f_{xc}(r, r') = \frac{\delta V_{xc}(r)}{\delta \rho(r')}
\]

Such an approach is known as the adiabatic approximation. If the excited state corresponds to the promotion of a single electron, the adiabatic approximation is applicable and calculated transition frequencies are quite accurate. However, if there is a promotion of two electrons taking place, the adiabatic approximation works very poorly because the underlying equations have no solutions, that correspond to the promotion of two particles.

1.2.3 Problems with Conventional Functionals

The conventional approach is to approximate the energy functional by some analytical expression of the density and its gradients. The effective potential can then be written in analytical form, and the Kohn-Sham equations can be solved readily. There are several levels of approximation for exchange-correlation functionals. The starting point for the
construction of approximate functionals is the Local Density Approximation (LDA), where
the energy is given through an integral of a local functional of the density. The second
level is Generalized Gradient Approximation (GGA) functionals, which improve upon
LDA by the addition of the dependence on the gradient of the density. The third level,
known as meta-GGA, contains also a dependence upon the gradients of the Kohn-Sham
orbitals. For the GGA and the meta-GGA there is the possibility to choose a form of a
functional. A number of different forms have been suggested. A standard way of choosing
the form of GGA and meta-GGA functionals is to satisfy a set of theorems, which are
known to be satisfied by the exact functional. Some functionals contain a set of parame-
ters to reproduce experimental data. Such functionals are called semiempirical. There are
also functionals which do not contain parameters but satisfy an extended set of theorems
(non-empirical functionals).

Kohn-Sham DFT with conventional functionals can produce very accurate results for
some properties. Values of the total energy, obtained with GGA are usually comparable
with some ab initio correlated results, like MBPT(2) or CCSD. This is a great advantage
of conventional DFT. However, the accuracy of GGA functionals is restricted by its
analytical form. Generalized gradient approximation exchange functionals cannot provide
the exact elimination of coulombic self-interaction of the Hartree energy. Since the
exchange energy is much larger than the correlation energy, an incomplete elimination of
self-interaction can significantly reduce the accuracy of the total energy. Particularly, the
impossibility to describe weakly-interacting systems, bounded mostly by dispersion forces,
arises from an incomplete elimination of self-interaction and the wrong behavior of the
exchange-correlation functionals with the separation of the system onto several fragments.

Although the exchange-correlation energies are quite accurate with GGA functionals,
the corresponding potentials are not nearly accurate, especially in the inter-shell and
asymptotic regions. As a consequence, the accuracy of the density is much lower than the
accuracy for the energy. Furthermore, the qualitatively incorrect potentials reduce the
usefulness of the Kohn-Sham orbitals and orbital energies for the calculation of ground-
state properties. Excitation energies and response properties are also very sensitive to the
form of the potential and their description with GGA are sometimes very inaccurate.

Some of the problems can be fixed without changing the functional form. Several
post-SCF corrections have been suggested to partially remove the self-interaction error.
For example, after the Kohn-Shan equations have been solved, a dispersion correction
to the energy is introduced to fix the long-range asymptotics of the exchange potential.
However, such corrections are very specific for the particular functional and the class of
the systems, and they are incompatible with each other. The extension of GGA to meta-
GGA does not fix all these problems. Their systematic and consistent resolution is needed
to go beyond GGA.

1.2.4 Orbital-Dependent Functionals

An alternative approach to DFT is to completely dismiss the conventional way of
expressing the exchange-correlation energy as an explicit functional of density. Instead,
the exchange-correlation energy is expressed in terms of orbitals and orbital energies,
yet, the potentials remain implicit functionals of the density. In Kohn-Sham DFT there
is a one-to-one mapping between the density and potential. Since orbitals are generated
by an effective potential through Kohn-Sham equations, there is a one-to-one mapping
between the set of orbitals and the density. Therefore, orbitals and orbital energies can be
considered as functionals of density.

In the case of orbital-dependent energy functionals corresponding exchange-
correlation potentials can not be calculated directly as functional derivatives with respect
to density. Instead, the chain rule should be used for the derivation of corresponding
potentials. Such potentials are equivalent to the corresponding potentials from optimized
effective potential (OEP) method. Therefore, the OEP-based methods constitute the basis
of DFT with orbital-dependent functionals.
The Hartree-Fock exchange functional provides an exchange part of orbital-dependent exchange-correlation potentials. Kohn-Sham DFT with OEP exchange potentials provides a superior results to all known density-dependent exchange functionals. To make OEP potentials useful for practical calculations it is necessary to have the correlation potential, which can be combined with it. Conventional GGA correlation functionals are developed together with the corresponding exchange potentials, which are very inaccurate. Because of this correlation potential of GGA compensates errors in the exchange part. In most cases GGA correlation potentials have an opposite sign to a nearly exact QMC potentials. The correcting terms incorporated into correlation potentials, so it is really difficult to extract the "real correlation part". So far, it is not surprising that combining GGA correlation potentials with OEP exchange potentials the associated results are inferior to exchange-only cases. Since conventional correlation functionals are not compatible with OEP, the development of orbital-dependent correlation functionals is necessary.

Ab initio DFT uses orbital-dependent correlation energy functionals from the rigorous wave-function methods. Since corresponding correlation potentials are derived from ab initio methods, they are compatible with OEP exchange potentials. Unlike conventional ones, ab initio functionals are systematically improvable, since one can always use a higher-level approximation to obtain a more accurate functional. They also have a well-defined limit represented by the FCI method.

1.2.5 Ab Initio Density Functional Theory

The main advantage of orbital-dependent energy functionals is the fact, that such functionals are known in analytical form. Particularly, the exchange functional can be written in following way

\[
E_x = \langle \Phi | V_{ee} | \Phi \rangle - E_H = -\frac{1}{2} \sum_{i,j} \langle \varphi_i \varphi_j | \varphi_j \varphi_i \rangle
\]
Here orbitals considered as implicit functionals of the density and the corresponding functional derivative will produce exact-exchange (EXX) potential.

The most important property of EXX functional is that, unlike conventional density functionals, it completely cancels the self-interaction component of Hartree energy, so the corresponding EXX potential will completely eliminate the self-interaction terms in Kohn-Sham equations. Thus, using the EXX functional and potential will avoid many problems, caused by the self-interaction error in conventional, approximated DFT for both energy and density. However, orbital dependence of EXX functional causes one complication. Since there is no explicit dependence upon density, potentials can not be written directly. Instead, one must rely on the chain rule, which takes into account the implicit dependence of orbitals on the density, expressing the derivative of interest through the product of known derivatives.

Ab initio orbital-dependent correlation energy functionals such as MBPT(2) can be used for the construction of correlation potentials. Such potentials exhibit correct $-C/r^4$ asymptotic behavior. It was also shown that MBPT(2) potentials are exact in the high-density limit and also very close to nearly exact QMC potentials. Alternatively, correlation potentials can be constructed from the so called density condition.
CHAPTER 2
INTERCONNECTION BETWEEN FUNCTIONAL DERIVATIVE AND EFFECTIVE OPERATOR APPROACHES TO AB INITIO DENSITY FUNCTIONAL THEORY

The use of the Kohn-Sham orbitals and orbital energies to construct an implicit density-dependent energy functional using, e.g., perturbation theory\[12, 13\] is a straightforward approach to the ab initio DFT. The corresponding Kohn-Sham potential can then be obtained by taking the functional derivative of the finite-order energy via the chain rule, that transforms the derivative with respect to the density into the derivative with respect to orbitals and orbital energies\[14\]. This leads to the Optimized Effective Potential\[13, 15\] equations which can be complicated already in second order\[13\].

Alternatively, one can determine the first and second order Kohn-Sham potential by requiring that the corresponding first and second order perturbative corrections to the reference density vanish. Unlike the functional derivative approach such a condition on the density can be described with standard many-body techniques. The recent work\[17\] uses diagrams to derive the second-order OEP equation in a systematic and compact fashion, while a second paper \[16\] does so algebraically.

Both the functional derivative and density (effective operator) approaches lead to exactly the same equation in the first order\[17\]. However, the functional derivative of the second energy involves a certain type of denominators that are not present in the density condition (effective operator approach). Still the terms involving such denominators can be transformed to match the density-based equation exactly. This caveat raises the question of whether the two approaches are equivalent in higher orders, or for different partitionings of the Hamiltonian.

2.1 Equations for the Exchange-Correlation Potential in the Functional Derivative Approach

To derive the equations in both approaches we first split the full electronic Hamiltonian into a perturbation and a zero-order Hamiltonian:

\[ H = H_0 + V \]  \hspace{1cm} (2-1)
Let us first consider the choice of \( H_0 \) as a sum of Kohn-Sham orbital energies:

\[
H_0 = \sum_{p=1}^{K} \epsilon_p \{a_p^+ a_p\}
\]  

(2–2)

where \( K \) is the number of orbitals. The brackets means that the product of second quantization operators are written in normal order. In the functional derivative method we define the exchange-correlation potential of the \( n \)-th order as:

\[
V_{xc}^{(n)}(r) = \frac{\delta E^{(n)}}{\delta \rho(r)}
\]  

(2–3)

where \( E^{(n)} \) is the energy of the \( n \)-th order of many-body perturbation theory. In single-reference many-body perturbation theory we have the energy of the \( n \)th order as an explicit functional of the orbitals. In the Görling-Levy approach this functional is considered to be a functional for the orbital energies also [14]:

\[
E^{(n)} = E^{(n)}(\varphi_1, \ldots, \varphi_n, \epsilon_1, \ldots, \epsilon_n)
\]

Another possible consideration [13], when orbital energies are considered to be a functionals over corresponding orbitals

\[
E^{(n)} = E^{(n)}(\varphi_1, \ldots, \varphi_n, \epsilon_1[\varphi_1], \ldots, \epsilon_n[\varphi_n])
\]  

(2–4)

is equivalent to the Görling-Levy [14] approach.

To construct the chain rule we should take into account the fact that the Kohn-Sham orbitals are functionals of \( V_s \):

\[
E^{(n)} = E^{(n)}(\varphi_1(V_s), \ldots, \varphi_n(V_s))
\]  

(2–5)

Then the Kohn-Sham potential can be considered to be a functional of \( \rho(r) \):

\[
E^{(n)} = E^{(n)}[\varphi_1(V_s(\rho(r))), \ldots, \varphi_n(V_s(\rho(r)))]
\]  

(2–6)
Variation of the energy can be presented in following form:

$$\delta E^{(n)} = \sum_{p} \int dr_2 \frac{\delta E^{(n)}}{\delta \varphi_p(r_2)} \delta \varphi_p(r_2)$$  \hspace{1cm} (2–7)

We can write down variations of the orbitals and the Kohn-Sham potential too:

$$\delta \varphi_p(r_2) = \int dr_1 \frac{\delta \varphi_p(r_2)}{\delta V_s(r_1)} \delta V_s(r_1)$$ \hspace{1cm} (2–8)

$$\delta V_s(r_1) = \int dr \frac{\delta V_s(r_1)}{\delta \rho(r)} \delta \rho(r)$$ \hspace{1cm} (2–9)

Using equations (2–8) and (2–9) we can rewrite the variation of the energy in the following form:

$$\delta E^{(n)} = \sum_{p} \int dr_2 \frac{\delta E^{(n)}}{\delta \varphi_p(r_2)} \int dr_1 \frac{\delta \varphi_p(r_2)}{\delta V_s(r_1)} \int dr \frac{\delta V_s(r_1)}{\delta \rho(r)} \delta \rho(r)$$ \hspace{1cm} (2–10)

Now we can write down the chain-rule\[13, 14]\ for the calculation of \(\delta V_{xc}^{(n)}\):

$$\frac{\delta E^{(n)}}{\delta \rho(r_1)} = \sum_{p} \int dr_2 \frac{\delta E^{(n)}}{\delta \varphi_p(r_2)} \int dr_3 \frac{\delta \varphi_p(r_2)}{\delta V_s(r_3)} \int dr \frac{\delta V_s(r_1)}{\delta \rho(r)}$$

Taking into account the fact that\[14]:

$$\frac{\delta \varphi_p(r)}{\delta V_s(r_1)} = \sum_{p,q \neq p} \frac{\varphi_p(r_1) \varphi_q(r_1) \varphi_q(r)}{\epsilon_p - \epsilon_q}$$ \hspace{1cm} (2–12)

$$\frac{\delta \epsilon_p}{\delta V_s(r)} = \varphi_p(r) \varphi_p(r)$$ \hspace{1cm} (2–13)

$$\frac{\delta \rho(r_1)}{\delta V_s(r_2)} = X(r_1, r_2) = 2 \sum_{a,i} \frac{\varphi_i(r_1) \varphi_a(r_1) \varphi_i(r_2) \varphi_a(r_2)}{\epsilon_i - \epsilon_a}$$ \hspace{1cm} (2–14)

it is possible to write an explicit expression for \(\delta V_{xc}^{(n)}(r)\) \[13\]

$$V_{xc}^{(n)}(r) = 2 \sum_{p,q \neq p} \int dr_2 \frac{\delta E^{(n)}}{\delta \varphi_p(r_2)} \varphi_q(r_2) \int dr_3 \frac{\varphi_p(r_3) \varphi_q(r_3)}{\epsilon_p - \epsilon_q} X^{-1}(r, r_3)$$ \hspace{1cm} (2–15)

Using the fact that

$$\int dr_2 X(r_1, r_2) X^{-1}(r_2, r_3) = \delta(r_1 - r_3)$$ \hspace{1cm} (2–16)
we can rewrite equation (2–15) as:

\[ \sum_{a,i} \varphi_a(r_1) \varphi_i(r_1) < \varphi_i | V_{xc}^n | \varphi_a > = \sum_{p,q \neq p} \frac{\delta E^{(n)}}{\delta \varphi_p} \varphi_p(r_1) \varphi_q(r_1) \frac{\varphi_p(r_3) \varphi_q(r_3)}{\varepsilon_p - \varepsilon_q} \]  

(2–17)

Using the fact that orbitals p and q can be occupied or unoccupied, we can separate the right-hand site of equation (2–17) into four parts:

\[ 2 \sum_{a,i} \varphi_a(r_1) \varphi_i(r_1) < \varphi_i | V_{xc}^n | \varphi_a > = \sum_{a,i} \frac{\delta E^{(n)}}{\delta \varphi_a} \varphi_i(r_3) \varphi_a(r_3) \frac{\varphi_i(r_1) \varphi_a(r_1)}{\varepsilon_i - \varepsilon_a} + \]

\[ + \sum_{a,i} \frac{\delta E^{(n)}}{\delta \varphi_i} \frac{\varphi_i(r_3) \varphi_a(r_3)}{\varepsilon_a - \varepsilon_i} \frac{\varphi_i(r_1) \varphi_a(r_1)}{\varepsilon_i - \varepsilon_i} + \]

\[ + \sum_{a,b \neq a} \frac{\delta E^{(n)}}{\delta \varphi_a} \frac{\varphi_a(r_3) \varphi_b(r_3)}{\varepsilon_a - \varepsilon_b} + c.c \]  

(2–18)

This form of equation (2–18) will be the basis for the formulation of the diagrammatic rules for taking functional derivatives and for making the connection with an effective operator approach to the OEP-MBPT exchange-correlation potential.

### 2.2 Equations for the Exchange-Correlation Potential in an Effective Operator Approach

Let us consider a one-particle density operator in second-quantized form:

\[ \rho(r) = \sum_{p,q} < \varphi_p | \delta(r - r_1) | \varphi_q > a_p^+ a_q \]  

(2–19)

Using Wick theorem, we rewrite this operator in normal form with the Kohn-Sham determinant as the Fermi-vacuum:

\[ \rho(r) = \sum_{p,q} < \varphi_p | \delta(r - r_1) | \varphi_q > a_p^+ a_q + < \Phi_{KS} | \delta(r - r_1) | \Phi_{KS} >= \]

\[ = \sum_{p,q} < \varphi_p | \delta(r - r_1) | \varphi_q > a_p^+ a_q + \sum_{i=1}^{N_{occ}} |\varphi_i(r)|^2 \]  

(2–20)

The first member of the previous expression will be called the **density correction**:

\[ \Delta \rho(r) = \sum_{p,q} < \varphi_p | \delta(r - r_1) | \varphi_q > a_p^+ a_q \]  

(2–21)
Since the converged Kohn-Sham scheme gives an exact density, all corrections to this
density must be equal to zero[17]. This means, that if we construct an effective operator of
the density using MBPT, the correction to the density must vanish in any order. This is
the main idea of the effective operator approach. For the exchange-correlation potential of
first order we will have:

\[
< \Phi_{KS} | \Omega^{(1)} + \Delta \rho(r) \Omega^{(1)} | \Phi_{KS} > = (\Omega^{(1)} + \Delta \rho(r))_{Sc} + (\Delta \rho(r) \Omega^{(1)})_{Sc} = 0 \quad (2-22)
\]

This condition can be presented by diagram (2–23).

\[
\begin{array}{c}
\delta \\
2 \quad i \\
\Phi \\
\end{array} = 0 \quad (1) \quad (2-23)
\]

Using the fact that \( f_{pq} = \varepsilon_p \delta_{pq} + < \varphi_p | V_x^{HF} - V_x(\rho) - V_c | \varphi_q > \), we can extract our
desirable exchange potential. The correlation part is excluded to maintain first order, as the
correlation potential contains expressions of second and higher orders. Then the equation
for \( V_x \) can be diagrammatically represented by diagrams 2 and 3.

\[
\begin{array}{c}
\delta \\
\chi \quad i \\
2 \\
\end{array} = \begin{array}{c}
\delta \\
i \\
a \\
3
\end{array}
\]

For the second-order effective operator for the density correction we will use the
expression (2–24)

\[
< \Phi_{KS} | (\Omega^{(1)} + \Omega^{(2)} + \Delta \rho(r) (\Omega^{(1)} + \Omega^{(2)}) | \Phi_{KS} >= \\
= (\Omega^{(1)} + \Delta \rho(r))_{Sc} + (\Delta \rho(r) \Omega^{(1)})_{Sc} + \\
+ (\Omega^{(2)} + \Delta \rho(r))_{Sc} + (\Delta \rho(r) \Omega^{(2)})_{Sc} + (\Omega^{(1)} + \Delta \rho(r) \Omega^{(1)})_{Sc} = 0 \quad (2-24)
\]

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Hence, the diagrammatic representation for the second-order equation is presented by the diagrams (3)-(18) of equation (2-25).

Diagrammatic representation of potential, derived from the density condition will be used for the establishing interconnection with the functional derivative approach.
2.3 Interconnection in Arbitrary Order

2.3.1 Diagrammatic Functional Derivatives

For formulation of the rules we will use equation (2–18). The δ - function needs to be introduced according to equation (2–26):

\[
\delta = \sum_{p, q \neq p} \frac{\varphi_p(r) \varphi_q(r)}{\varepsilon_p - \varepsilon_q} = \delta - a_i \delta_{a_i} - \delta_{a_i} \delta_{a_i} + \delta_{a_i} \delta_{a_i} \tag{2–26}
\]

Brackets on the last two diagrams denote denominators. Expressions for the energy in MBPT consist of linear combinations of terms, which have products of molecular integrals in the numerators and product of differences of one-particle energies in the denominators, so it is easy to make a diagrammatic representation for such expressions. To take the functional derivatives from numerators, according to equation (2–18), all lines connected to some vertex must be disconnected from the corresponding place of linking, and when this is done, a new line (corresponding to occupied or unoccupied orbitals) must be inserted. In the final step contraction with the corresponding δ - function must be provided. All lines corresponding to denominators are still unchanged. This procedure must be provided for all vertices, because when we take functional derivatives from products of functions, we have a sum of products, according to rules for taking derivatives. If a new diagram changes its sign, a minus sign must be assigned to this diagram.

When functional derivatives from denominators are taken, it is more suitable to use equation (2–13). The most general form for the denominator can be represented by the following formula:

\[
Den = \prod_{\alpha} \left( \sum_{i=1}^{K_\alpha} \varepsilon_i^{\alpha \text{o cc}} - \sum_{j=1}^{K_\alpha} \varepsilon_j^{\alpha \text{unocc}} \right) \tag{2–27}
\]
Using equation (2–13) it is possible to write down the functional derivatives from some denominator in the general form:

\[
\frac{\delta \text{Den}}{\delta V_s} = \left( \sum_{i=1}^{K_1} |\varphi_{\text{occ}}^i|^2 - \sum_{j=1}^{K_1} |\varphi_{\text{unocc}}^j|^2 \right) \prod_{\alpha, \alpha \neq 1} \left( \sum_{i=1}^{K_\alpha} \epsilon_{\text{occ}}^i - \sum_{j=1}^{K_\alpha} \epsilon_{\text{unocc}}^j \right) + \ldots + 
\]

\[
\left( \sum_{i=1}^{K_\beta} |\varphi_{\text{occ}}^i|^2 - \sum_{j=1}^{K_\beta} |\varphi_{\text{unocc}}^j|^2 \right) \prod_{\alpha, \alpha \neq \beta} \left( \sum_{i=1}^{K_\alpha} \epsilon_{\text{occ}}^i - \sum_{j=1}^{K_\alpha} \epsilon_{\text{unocc}}^j \right)
\]

\[ (2–28) \]

Now it is possible to write down a term which includes the functional derivative from the denominator:

\[
\frac{\text{Nom} \ \delta \text{Den}}{(\text{Den})^2 \ \delta V_s} = 
\]

\[
\sum_{\beta} \frac{\text{Nom}(\sum_{i=1}^{K_\beta} |\varphi_{\text{occ}}^i|^2 - \sum_{j=1}^{K_\beta} |\varphi_{\text{unocc}}^j|^2) \prod_{\alpha, \alpha \neq \beta}(\sum_{i=1}^{K_\alpha} \epsilon_{\text{occ}}^i - \sum_{j=1}^{K_\alpha} \epsilon_{\text{unocc}}^j)}{(\sum_{i=1}^{K_\beta} \epsilon_{\text{occ}}^i - \sum_{j=1}^{K_\beta} \epsilon_{\text{unocc}}^j)^2 \prod_{\alpha, \alpha \neq \beta}(\sum_{i=1}^{K_\alpha} \epsilon_{\text{occ}}^i - \sum_{j=1}^{K_\alpha} \epsilon_{\text{unocc}}^j)}
\]

\[ (2–29) \]

We now have the possibility to formulate how to take functional derivatives from denominators. To take functional derivatives from denominators, all diagrams, where one of the lines is doubled and between these lines which arise from doubling, the corresponding diagonal \( \delta \)-function is inserted. This procedure must be provided for all horizontal lines on the diagram and for all the contours the lines cross.

### 2.3.2 Diagrammatic Functional Derivatives in Second-Order Many-Body Perturbation Theory

Direct interconnection in first order is clear from diagram’s 2 and 3. The left-hand side of equation (2–17) is equal to diagram 2, the right-hand site is equal to diagram 3 when the functional derivative has been taken from the expression for the exchange energy.

The diagrammatic expression for the second-order energy in the general case has the form[1]:

\[
E^{(2)} = \begin{array}{c}
\text{F} \\
\text{a}
\end{array} + 2 \begin{array}{c}
\text{F} \\
\text{i} \\
\text{a} \\
\text{j} \\
\text{b}
\end{array} + 2 \begin{array}{c}
\text{F} \\
\text{i} \\
\text{a} \\
\text{j} \\
\text{b}
\end{array}
\]

\[ (2–30) \]
Consider the second and third diagram in the energy expression. For the sake of simplicity
only non-equivalent diagrams will be given. Taking functional derivatives with respect to
occupied orbitals we will have equation (2–31)

\[
\begin{align*}
&\left( \sum_{\text{occupied orbitals}} \langle i | a | j \rangle \right) \left( \left( \sum_{\text{occupied orbitals}} \langle i | a | j \rangle \right) + \left( \sum_{\text{occupied orbitals}} \langle i | a | j \rangle \right) \right) \\
\end{align*}
\]  

(2–31)

Inserting the lines of unoccupied orbitals and making contractions with the \( \delta \) - function,
diagrams 4 and 8 of equation (2–25) will be obtained (2–32):

\[
\begin{align*}
&\left( \sum_{\text{unoccupied orbitals}} \langle i | b | c \rangle \delta_{a_i b_j c_k} \right) + \left( \sum_{\text{unoccupied orbitals}} \langle i | b | c \rangle \delta_{a_i b_j c_k} \right) \\
\end{align*}
\]  

(2–32)

When functional derivatives are taken with respect to unoccupied orbitals and occupied
orbitals are inserted, diagrams 5 and 9 of equation (2–25) will be obtained. When this
procedure is done for the lower vertex, complex conjugate diagrams will be obtained
and we will have the same number of diagrams of this sort as in the effective operator
approach.

When functional derivatives are taken with respect to occupied orbitals for the
upper and lower vertexes and an occupied line is inserted, we have the diagrams, given by
equation (2–33)

\[
\begin{align*}
&\left( \sum_{\text{occupied orbitals}} \langle i | k | j \rangle \delta_{a_i b_j k} \right) + \left( \sum_{\text{occupied orbitals}} \langle i | k | j \rangle \delta_{a_i b_j k} \right) + \left( \sum_{\text{occupied orbitals}} \langle i | k | j \rangle \delta_{a_i b_j k} \right) + \left( \sum_{\text{occupied orbitals}} \langle i | k | j \rangle \delta_{a_i b_j k} \right) \\
\end{align*}
\]  

(2–33)

“Bracket-type” denominator means the difference \( \varepsilon_i - \varepsilon_k \). Summation of the fist two
diagrams according to the Frantz-Mills theorem[18] and the same procedure for the second
two diagrams gives the diagrams of equation (2–34)

\[
\begin{align*}
\delta_k & \begin{array}{c}
\kappa
\end{array} \begin{array}{c}
\iota
\end{array} \begin{array}{c}
\kappa
\end{array} \\
2 & \begin{array}{c}
\delta
\end{array} \begin{array}{c}
\iota
\end{array} \begin{array}{c}
\kappa
\end{array} + 2 \begin{array}{c}
\delta
\end{array} \begin{array}{c}
\kappa
\end{array} \begin{array}{c}
\iota
\end{array} \begin{array}{c}
\kappa
\end{array}
\end{align*}
\]  

(2–34)

On the two diagrams we impose the restriction \( i \neq k \). To make a direct correspondence with diagrams 7 and 11 we need to add diagrams that arise from taking functional derivatives from denominators (2–35)

\[
\begin{align*}
\delta_k & \begin{array}{c}
\kappa
\end{array} \begin{array}{c}
\iota
\end{array} \begin{array}{c}
\kappa
\end{array} \\
2 & \begin{array}{c}
\delta
\end{array} \begin{array}{c}
\kappa
\end{array} \begin{array}{c}
\iota
\end{array} \begin{array}{c}
\kappa
\end{array} + 2 \begin{array}{c}
\delta
\end{array} \begin{array}{c}
\kappa
\end{array} \begin{array}{c}
\iota
\end{array} \begin{array}{c}
\kappa
\end{array}
\end{align*}
\]  

(2–35)

After these diagrams are added to the previous two, we will have a direct correspondence with diagrams 7 and 11. When functional derivatives are taken with respect to the unoccupied orbitals and an unoccupied line inserted, the same procedure will give a direct correspondence with diagrams 6 and 10 of equation (2–25).

Now consider the first diagram for the second-order energy expression. The procedure for taking functional derivatives from the right side of the vertex, which do not contain a closed F-ring are absolutely the same as in the case of other second and third diagrams in the energy expression. When such functional derivatives are taken, we have four diagrams corresponding to diagrams 12-15. To take functional derivatives from the F-rings, the first diagram in the energy expression must be represented with more detail, taking into account that \( f = h + J - K \), in following the form (2–36)

\[
\begin{align*}
\begin{array}{c}
\overline{F}
\end{array} & \begin{array}{c}
\overline{X}
\end{array} + \begin{array}{c}
\overline{X}
\end{array} + 2 \begin{array}{c}
\overline{X}
\end{array} + 2 \begin{array}{c}
\overline{X}
\end{array} + 2 \begin{array}{c}
\overline{X}
\end{array} + 2 \begin{array}{c}
\overline{X}
\end{array}
\end{align*}
\]  

(2–36)
When rules for taking functional derivatives diagrammatically are applied to this set of diagrams, we will have the next set of diagrams (2–37)

\[ \delta F + 2 \delta F + 2 \delta F + 2 \delta \]

The first two diagrams are equal to diagram 16; the third and fourth equal to diagrams 17 and 16 respectively. Since the left-hand site of eq.12 can be represented by diagram 3, we have an exact equivalence between the functional derivative and the effective operator approaches in the first and second order for the "Kohn-Sham" partitioning of the Hamiltonian.

2.3.3 Interconnection in Higher Orders

Equations for the effective-operator approach in the n-th order of MBPT have the form (2–38)

\[ \langle \Phi_{KS} | (\Omega^{(1)} + \ldots + \Omega^{(n)}) \Delta \rho(r)(\Omega^{(1)} + \ldots + \Omega^{(n)}) | \Phi_{KS} \rangle = \sum_{k=0}^{n} (\delta \Omega^{(k)} + \Omega^{(n-k)})_{Sc} = 0 \]  

This equation tells us that we need to collect and equate to zero the sum of all possible combinations of wave operators and density correction operators, and these combinations must be of n-th order. The same result should correspond to taking functional derivatives from all energy diagrams of n-th order.

**Statement 1**: When functional derivatives from some vertex of a diagram are taken with respect to an occupied (unoccupied) orbital, and a line, which corresponds to an unoccupied (occupied) orbital inserted, we always will have diagrammatic expressions which correspond to part of \( \sum_{k=0}^{n} (\delta \Omega^{(k)} + \Omega^{(n-k)})_{Sc} \).

**Proof**: When functional derivatives are taken with respect to an occupied (unoccupied) orbital, and a line which corresponds to an unoccupied (occupied) orbital is inserted, we always have a contraction of the delta function with some fully connected...
diagrammatic expression. All lines which correspond to denominators are still unchanged, except there is one extra denominator from the delta-function. If the functional derivative had been taken with respect to the highest or lowest vertex in the energy diagram, the resulting diagram corresponds to the product $\delta \Omega^{(n)}$, in the nth-order of perturbation theory.

After applying the same procedure to some intermediate vertex, we have an expression which contains $n-1$ denominators and one extra denominator from the delta-function. To transform the resulting diagram into the product of a delta-function and two wave operators, we need one extra line, which cross all lines at its level. Such a line can be obtained, using the Frantz-Mills[18] factorization theorem. Since all initial horizontal lines cross all lines, which go up from lower lying vertexes, it is possible to represent the diagrams, which appear after applying the Frantz-Mills[18] theorem in the form (2–39)

$$\delta \Omega^{(k)} + \Omega^{(n-k)}$$

(2–39)

Each $k$ corresponds to some time version. When functional derivatives will be taken from all vertexes in all diagrams, we will have all possible contractions of the density correction operator, which have lines going up or down, with products of wave operators. So we have part of $\sum_{k=0}^{n} (\delta \Omega^{(k)} + \Omega^{(n-k)})_{Sc}$.

For example, in third order we will have:

(2–40)

The diagram on the left-hand side is the result of taking functional derivatives from typical energy diagrams of third order. Applying the factorization theorem[18] to the right-hand side we will have the same result as on the left-hand side of this relation. The
first member of the right-hand side corresponds to $\delta \Omega^{(3)}$, while the second corresponds to $\delta \Omega^{(1)} + \Omega^{(2)}$.

To finally establish the interconnection between the two approaches, we need to show that it is possible to transform diagrams which contain "bracket-type denominators to standard diagrams. In a previous subsection this procedure was described for the case where one horizontal line crosses the contour in the diagram, which corresponds to the energy in second order MBPT. We need to prove, that energy diagrams, which contain contours crossed by m lines, after taking the functional derivative which respect to unoccupied (occupied) orbitals and inserting lines of unoccupied (occupied) orbitals; can be transformed to linear combination of m diagrams which do not contain "bracket-type" denominators.

Consider the following diagram (2–41):

\[
\text{(2–41)}
\]

Numbers on lines show the conditional number of lines which are entered for simplicity of further manipulations. The desirable sum of diagrams has the form (2–42)

\[
\text{(2–42)}
\]

Together with diagrams which correspond to functional derivatives from denominators, this set of diagrams forms products like $\Omega^{(k)} + \delta \Omega^{(l)}$, where $k+l$ equals the order of MBPT.
After cancellation of all equivalent terms, we have the expressions (2–43)

\[
\sum \frac{\text{Nom}}{(\epsilon_k + A_1)(\epsilon_l + A_1)\ldots(\epsilon_k + A_m)} + \\
\sum \frac{\text{Nom}}{(\epsilon_l + A_1)(\epsilon_k + A_2)(\epsilon_l + A_2)\ldots(\epsilon_k + A_m)} + \ldots + \sum \frac{\text{Nom}}{(\epsilon_l + A_1)\ldots(\epsilon_l + A_m)(\epsilon_k + A_m)}
\]

(2–43)

In these expressions Nom means numerator, $A_i$ means the rest of the terms, which are present in denominators. After multiplication and division by $(\epsilon_k - \epsilon_l)$ we have (2–44)

\[
\sum \frac{\text{Nom}(\epsilon_k - \epsilon_l + A_1 - A_1)}{(\epsilon_k - \epsilon_l)(\epsilon_l + A_1)(\epsilon_k + A_1)\ldots(\epsilon_k + A_m)} + \\
\sum \frac{\text{Nom}(\epsilon_k - \epsilon_l + A_2 - A_2)}{(\epsilon_k - \epsilon_l)(\epsilon_l + A_1)(\epsilon_k + A_2)\ldots(\epsilon_k + A_m)} + \ldots + \sum \frac{\text{Nom}(\epsilon_k - \epsilon_l + A_m - A_m)}{(\epsilon_k - \epsilon_l)(\epsilon_l + A_1)\ldots(\epsilon_l + A_m)(\epsilon_k + A_m)} = \\
- \sum \frac{\text{Nom}}{(\epsilon_k - \epsilon_l)(\epsilon_l + A_1)(\epsilon_k + A_2)\ldots(\epsilon_k + A_m)} - \\
- \sum \frac{\text{Nom}}{(\epsilon_k - \epsilon_l)(\epsilon_k + A_1)(\epsilon_k + A_2)\ldots(\epsilon_k + A_m)} - \\
+ \sum \frac{\text{Nom}}{(\epsilon_k - \epsilon_l)(\epsilon_l + A_1)(\epsilon_l + A_2)(\epsilon_l + A_3)\ldots(\epsilon_k + A_m)} - \\
- \sum \frac{\text{Nom}}{(\epsilon_k - \epsilon_l)(\epsilon_l + A_1)(\epsilon_l + A_2)(\epsilon_k + A_3)\ldots(\epsilon_k + A_m)} + \ldots + \sum \frac{\text{Nom}}{(\epsilon_k - \epsilon_l)(\epsilon_l + A_1)\ldots(\epsilon_l + A_m)} - \\
- \sum \frac{\text{Nom}}{(\epsilon_k - \epsilon_l)(\epsilon_l + A_1)\ldots(\epsilon_k + A_m)}
\]

(2–44)

After cancellation of all equivalent terms, we have the expressions (2–45)

\[
- \sum \frac{\text{Nom}}{(\epsilon_k - \epsilon_l)(\epsilon_k + A_1)\ldots(\epsilon_k + A_m)} - \sum \frac{\text{Nom}'}{(\epsilon_k - \epsilon_l)(\epsilon_k + A_1)\ldots(\epsilon_k + A_m)}
\]

(2–45)
where Nom' is the numerator, with interchanged indexes k and l. These expressions can be represented by the following two diagrams (2–46).

![Diagram](image)

(2–46)

Namely these two diagrams will appear after taking functional derivatives using diagrammatic rules for taking functional derivatives. Proof for the case where functional derivatives are taken with respect to unoccupied orbitals is the complete analog of this one. Hence, we can formulate a second statement.

**Statement 2:** When functional derivatives from some vertex of a diagram are taken with respect to occupied (unoccupied) orbitals, and a line which corresponds to occupied (unoccupied) orbital inserted, together with diagrams which arise from taking functional derivatives from denominators; we always have diagrammatic expressions, which corresponds to part of \( \sum_{k=0}^{n} (\delta \Omega^{(k)} + \Omega^{(n-k)})_{Sc} \).

This statement is a direct corollary of the above proved statement about "bracket-type" denominators and statement 1. Since we have correspondence in the second and n-th order, using the method of mathematical induction, it is possible to prove, that the correspondence takes place in all orders (finite or infinite).

### 2.3.4 Interconnection in Infinite Order

It should be noted that summation of perturbation corrections to the energy and the wave functions up to infinite order provide correspondence with the full CI:

\[
\sum_{n=0}^{\infty} E^{(n)} = E^{(FCI)} \\
\sum_{n=0}^{\infty} \Psi^{(n)} = \Psi^{(FCI)}
\]

(2–47)
Using the effective operator approach it is possible to define $V^{(n)}_{xc}$ in all possible orders. This procedure for an infinite sum of orders gives $V_{xc}$. Inserting this potential into the Kohn-Sham equations, we can find $\rho^{(\infty)}$, which corresponds to the one-particle density in the full CI method. The same density could be used in a method like Zhao-Morrison-Parr (ZMP)\cite{19} to extract the corresponding exchange-correlation potential. Since the full CI energy does not depend upon the choice of orbital basis set, the OEP procedure\cite{13, 15} cannot be used directly for this case. The infinite sum of all energy corrections does not depend upon choice of orbital basis set, but each term of this sum does depend upon the choice of orbitals. This fact enables us to consider all term of the infinite sum of energy corrections as orbital-dependent functionals. After the construction of the set $V^{(1)}_{xc} \ldots V^{(\infty)}_{xc}$ andsummation up to infinity, we will have the exchange-correlation potential which corresponds to the full CI. Using the equivalence of the functional derivative and the effective operator approach, it is possible to conclude that after summation of this set of potentials, we again will have the same result as in the effective operator approach. Redefined in such a way, the OEP procedure\cite{13, 15} for the full CI energy produces the same density as the ZMP method\cite{19} would from full CI.
CHAPTER 3
AB INITIO TIME-DEPENDENT DENSITY FUNCTIONAL THEORY EMPLOYING
SECOND-ORDER MANY-BODY PERTURBATION THEORY OPTIMIZED
EFFECTIVE POTENTIAL

The time-dependent OEP exchange-only method in the adiabatic approximation
has been previously derived [20] and implemented for molecules by Hirata et. al [21].
Numerical results in that work show a reasonable description of both valence and Rydberg
excited states, partly due to the correct asymptotic behavior of the exchange potential,
but also due to the elimination of the self-interaction error. In particular, OEP-TDDFT
is superior to standard approaches like TDDFT based upon local density approximation
(LDA) or Becke-Lee-Yang-Parr (BLYP) functionals. Similarly, exchange-only OEP with
exact local exchange (EXX)[22, 23] has been shown to greatly improve band-gaps in
polymers [23].

Another advantage of OEP based methods is that since virtual orbitals in the
exchange-only DFT as well as occupied orbitals are generated by a local potential,
which corresponds to the N-particle system, the differences between orbital energies of
virtual and occupied orbitals offer a good zeroth-order approximation to the excitation
energies [16, 17]. This is not possible in the case of Hartree-Fock theory, where occupied
orbitals are generated by an N-1 particle potential and the energies of unoccupied orbitals
come from N-electron potential, and thereby, approximate electron affinities.

Once OEP correlation is added [13, 17], the essential new element in the time-
dependent DFT scheme is the exchange-correlation kernel, which in the adiabatic approx-
imation is defined as a functional derivative of the exchange-correlation potential with
respect to the density [20]:

\[ f(r_1, r_2) = \frac{\delta \hat{V}_{xc}(r_1)}{\delta \rho(r_2)} \]  

(3-1)

Hence, in this paper we will derive the kernel for the OEP-MBPT(2) correlation potential,
when we use the standard KS \( H_0 \), \( H_0 = \sum_i h_{ki}(i) \). In prior papers [16, 17] this has
been called OEP Kohn-Sham (KS) to distinguish it from other choices for \( H_0 \). It is
also the choice of Görling and Levy\cite{14, 24}. Only for this choice is there an immediate correspondence between the functional derivative and KS density condition that a single determinant provides the exact density\cite{24}. The other choices for $H_0$ lead to what is called \textit{ab initio} DFT \cite{16, 17} and becomes a better separation of hamiltonian into $H_0 + V'$. Its convergence for orbital-dependent perturbation approximations to the correlation energy functionals are considerably better behaved compared to the KS choice that frequently causes divergence. Nevertheless, in this first application we will adhere to the standard KS separation, where the potential and kernel are functional derivatives.

The traditional way of deriving kernels and potentials is to tediously derive all terms with the use of the chain-rule for functional differentiation. Yet, even the exchange-only kernel has a complicated structure in OEP, and its further extension to include correlation would be almost impossible. To avoid the use of traditional methods, an effective diagrammatic formalism for taking functional derivatives has been developed and implemented.

3.1 Diagrammatic Construction of the Exchange-Correlation Kernels

3.1.1 Formalism

The adiabatic (frequency-independent) approximation to the kernel of the nth order is defined as (3–2)

$$f^{(n)}(r_1, r_2) = \frac{\delta V_{xc}^{(n)}(r_1)}{\delta \rho(r_2)} = \int dr_3 \frac{\delta V_{xc}^{(n)}(r_1)}{\delta \rho_3} X^{-1}(r_3, r_2)$$

The exchange-correlation potential of nth order is then defined through the chain-rule by the following formula\cite{13} (3–3)

$$V_{xc}^{(n)}(r) = \sum_{p,q \neq p} \int dr_2 \frac{\delta E^{(n)}}{\delta \varphi_p(r_2)} \varphi_q(r_2) \int dr_3 \frac{\varphi_p(r_3) \varphi_q(r_3)}{\varepsilon_p - \varepsilon_q} X^{-1}(r, r_3) + c.c$$
where the c.c means the complex-conjugate. Inserting equation (3–3) into (3–2) we obtain

\[
f^{(n)}(r_1, r_2) = \sum_{p,q \neq p} \sum_{r \neq r} \int dr_4 \frac{\delta}{\delta \varphi_p(r_4)} \left( \int dr_5 \frac{\delta E^{(n)}}{\delta \varphi_p(r_5)} \varphi_s(r_5) \right) \times \\
\times \int dr_6 \frac{\varphi_r(r_6) \varphi_s(r_6)}{\varepsilon_r - \varepsilon_s} X^{-1}(r_1, r_6) + c.c) \varphi_q(r_4) \times \\
\times \int dr_3 \frac{\varphi_p(r_3) \varphi_q(r_3)}{\varepsilon_p - \varepsilon_q} X^{-1}(r_2, r_3) + c.c
\]

(3–4)

This may be rewritten as (3–5)

\[
f^{(n)}(r_1, r_2) = \sum_{p,q \neq p} \int dr_3 \frac{\delta}{\delta V_s(r_3)} \left( \int dr_5 \frac{\delta E^{(n)}}{\delta \varphi_p(r_5)} \varphi_q(r_5) \right) \times \\
\times \int dr_6 \frac{\varphi_p(r_6) \varphi_q(r_6)}{\varepsilon_p - \varepsilon_q} X^{-1}(r_1, r_6) + c.c)X^{-1}(r_2, r_3) + c.c
\]

(3–5)

Equation (3–5) can be made more explicit,

\[
f^{(n)}(r_1, r_2) = \sum_{p,q \neq p} \int dr_3 X^{-1}(r_2, r_3) \left( \frac{\delta}{\delta V_s(r_3)} \right) \left( \int dr_5 \frac{\delta E^{(n)}}{\delta \varphi_p(r_5)} \varphi_q(r_5) \right) \times \\
\times \int dr_6 \frac{\varphi_p(r_6) \varphi_q(r_6)}{\varepsilon_p - \varepsilon_q} X^{-1}(r_1, r_6) + c.c) + \sum_{p,q \neq p} \int dr_3 X^{-1}(r_2, r_3) \times \\
\times \int dr_5 \frac{\delta E^{(n)}}{\delta \varphi_p(r_5)} \varphi_q(r_5) \int dr_6 \frac{\varphi_p(r_6) \varphi_q(r_6)}{\varepsilon_p - \varepsilon_q} \frac{\delta X^{-1}(r_1, r_6)}{\delta V_s(r_3)} + c.c
\]

(3–6)

Using the fact that[14]

\[
\frac{\delta X^{-1}(r_1, r_2)}{\delta V_s(r_3)} = - \int dr_5 \int dr_6 X^{-1}(r_1, r_5) \frac{\delta X(r_5, r_6)}{\delta V_s(r_3)} X^{-1}(r_6, r_2)
\]

(3–7)

it is possible to rewrite equation (3–6) in the following form (3–8)

\[
f^{(n)}(r_1, r_2) = \int dr_3 \int dr_6 X^{-1}(r_1, r_3) h(r_3, r_6) X^{-1}(r_6, r_2)
\]

(3–8)

Taking into account equation(3–3) we have the explicit expression (3–9) for \( h(r_3, r_6) \)

\[
h(r_3, r_6) = \frac{\delta}{\delta V_s(r_3)} \left[ \sum_{p,q \neq p} \int dr_5 \frac{\delta E^{(n)}}{\delta \varphi_p(r_5)} \varphi_q(r_5) \frac{\varphi_p(r_6) \varphi_q(r_6)}{\varepsilon_p - \varepsilon_q} \right] - \\
- \int dr_5 \frac{V^{(n)}_{2c}(r_5) \delta X(r_5, r_6)}{\delta V_s(r_3)} + c.c
\]

(3–9)
Equation (3–9) will be used as the basis for the diagrammatic procedure for taking functional derivatives from the OEP-MBPT exchange-correlation potentials. The first term of equation (3–9) contains the functional derivative with respect to the potential, from an expression which already includes the functional derivative of the energy with respect to the same potential.

Diagrammatic rules for taking functional derivatives from numerators of diagrams are the following:

- Detach the line from the vertex
- Insert parts of the $\hat{\delta}$-function (2–26) to get the fully connected diagram
- Repeat the procedure for all vertices in all diagrams which contribute to the exchange-correlation energy

To take the functional derivative of the denominators, the denominator line should be doubled and diagonal expressions of the last two parts of the $\hat{\delta}$-function (2–26) should be inserted between doubled lines for all lines which are intersected by the denominator line. This procedure should be done for all possible denominator lines. The rules of interpretation are the same as for the usual Goldstone diagrams, except the numerical factor should be taken from the initial diagram when functional derivatives are taken.

After taking the functional derivatives from the exchange-correlation with respect to the potential using diagrammatic rules, a set of diagrams, containing the $\hat{\delta}$-function vertex will appear. To get the first element of equation (3–9), it is necessary to apply diagrammatic rules to the set of functional derivative diagrams one more time. After that we will have a set of diagrams containing two $\hat{\delta}$-functions, which are necessary for the construction of the exchange-correlation kernels.

Taking into account equation (2–14), the second term of equation (3–9) can be rewritten in the following way (3–10)

\[- \int dr_5 \frac{V_{xc}^{(n)}(r_5)\delta X(r_5,r_6)}{\delta V_s(r_3)} = -2\sum_{a,i} \int dr_5 \frac{\delta}{\delta V_s(r_3)} \left[ \varphi_i(r_5)\varphi_a(r_5)\varphi_i(r_6)\varphi_a(r_6) \right] \] (3–10)
The expression, which is supposed to be differentiated with respect to the potential on the right-hand side of equation (3–10) can be represented by diagram (V) (3–11)

![Diagram (V)](V)

(3–11)

The functional derivatives from diagram (V) produce the set of diagrams (V1)-(V6) of set (3–12)

![Diagrams (V1)-(V6)](3–12)

During the derivation of diagrams (V1)-(V4), diagrams containing "bracket-type" denominators will appear, because one of the steps in the diagrammatic rules of differentiation requires detaching the unoccupied line from diagram V and inserting the last two parts of the \( \hat{\delta} \)-function (2–26). Such diagrams can be transformed into a set of regular diagrams, using the diagrammatic relation (3–13). This relation shows us that for the transformation to regular diagrams it is necessary to double each of the denominator lines and insert the last two members of the \( \hat{\delta} \)-function (2–26), subject to the restricted summation, \( l \neq k \). We use the same procedure for the case of occupied orbitals.

![Diagram (D1)](D1)

(3–13)
After the transformation of irregular diagrams and adding the functional derivatives from the denominator of diagram (V), diagrams (V1)-(V4) will appear. Using diagrammatic expressions for the first member of equation (3–9) and diagrams (V1)-(V6) it is possible to build the exchange-correlation kernels to any order.

### 3.1.2 An Example: Diagrammatic Derivation of Exchange-Only Kernel

The kernel for the exchange-only case was initially derived by Görling [20], and then rederived and initially implemented by Hirata et. al [21]. Such a derivation requires much effort. Here we offer a facile derivation with the diagrammatic formalism.

The exchange energy \( E_x = -\frac{1}{2} \sum_{i,j} < ij | ji > \) can be represented by diagram (3–14).

\[
E_x = \begin{array}{c}
\text{(EX)} \\
\end{array}
\]  

(3–14)

After taking the first functional derivative with respect to \( V_s \) we will have the diagram (3–15).

\[
\frac{\delta E_x}{\delta V_s} = 2 \begin{array}{c}
i \\
\delta_j \\
a \\
\end{array}
\]  

(VX)  

(3–15)

After that the diagrammatic rules must be applied one more time to get the second functional derivative, as is necessary according to equation (3–9). After taking the second functional derivatives we will have diagrams (FX1)-(FX8) of the set (3–16)

\[
\begin{align*}
\text{(FX1)} & \quad \text{(FX2)} & \quad \text{(FX3)} & \quad \text{(FX4)} & \quad \text{(FX5)} & \quad \text{(FX6)} & \quad \text{(FX7)} & \quad \text{(FX8)} \\
\end{align*}
\]  

(3–16)

After the addition of diagrams (V1)-(V6) we will have all the diagrams necessary for building the exchange-only kernel. During the interpretation of diagrams (V1)-(V6) the
potential vertex should be the matrix element $\langle \varphi_p | V_2 | \varphi_q \rangle$ and a factor -2 must be added according to equation (3–10). Interpretation of diagrams (FX1)-(FX8) and (V1)-(V6) gives us the expression (3–17)

$$h(r_3, r_6) = -2 \sum_{i,j,a,b} \frac{\langle ia|jb \rangle - \langle ij|ba \rangle}{(\epsilon_i - \epsilon_a)(\epsilon_j - \epsilon_b)} \sum_{i,j,a,b} \frac{\langle aj|ji \rangle - \langle ai|ji \rangle}{(\epsilon_i - \epsilon_a)(\epsilon_j - \epsilon_b)}$$

Expression (3–17) for $h(r_3, r_6)$ exactly corresponds to the expression, obtained by Hirata et. al, but the diagrammatic derivation requires far less effort and is unambiguous in terms of signs and numerical factors. Since all the diagrams contain only one contour, it is possible to make summations in equation (3–17) only over spatial orbitals, and, as a result $f_{\alpha\alpha}(r_1, r_2)$ and $f_{\beta\beta}(r_1, r_2)$ will appear separately. The exchange-only kernel does not contain the $f_{\alpha\beta}(r_1, r_2)$ part, which is a critical difference between the exchange and correlation kernels.
### 3.2 Kernel for the Second-Order Optimized Effective Potential Many-Body Perturbation Theory Correlation Potential

For the derivation of the second-order exchange-correlation kernel we require functional derivatives of the second-order correlation energy with respect to $V_s$. These functional derivatives can be represented by diagrams (VC1)-(VC15) of (3–18).

\begin{align*}
\text{(VC1)} & \quad \text{(VC2)} & \quad \text{(VC3)} & \quad \text{(VC4)} \\
\text{(VC5)} & \quad \text{(VC6)} & \quad \text{(VC7)} & \quad \text{(VC8)} \\
\text{(VC9)} & \quad \text{(VC10)} & \quad \text{(VC11)} & \quad \text{(VC12)} & \quad \text{(VC13)} & \quad \text{(VC14)} & \quad \text{(VC15)}
\end{align*}

Diagrams (VC1), (VC2), (VC5), (VC6) and (VC15) of (3–18) have an external factor 4, diagrams (VC9) and (VC10) have no factor, while the rest of the diagrams have a factor of 2. To get the correlation kernel diagrams we need to take functional derivatives with respect to the potential from diagrams (V1)-(V15). After applying the diagrammatic rules to diagram (VC1) and the use of relation (3–13), diagrams (VC1-1)-(VC1-16) of sets (3–19) and (3–20) will appear.

\begin{align*}
\text{(VC1-1)} & \quad \text{(VC1-2)} & \quad \text{(VC1-3)} & \quad \text{(VC1-4)} & \quad \text{(VC1-5)} & \quad \text{(VC1-6)} & \quad \text{(VC1-7)}
\end{align*}

(3–18)
Differentiation of diagram (VC2) produce diagrams (VC2-1)-(VC2-16) of set (3–21). These diagrams have the same skeleton structure, but different positions of indices.

After taking the functional derivatives from diagram (VC3) diagrams (VC3-1) - (VC3-14) (3–22) will appear.
When functional derivatives are taken from the diagram (VC4), diagrams (VC4-1)-(VC4-14) (3–23) will appear.

Diagram (VC5) produces diagrams (VC5-1)-(VC5-16) (3–24) after differentiation.

Differentiation of diagram (VC6) generate diagrams (VC6-1)-(VC6-16) (3–25),
while diagram (VC7) gives diagrams (VC7-1)-(VC7-14) (3–26).

Finally, diagram (VC8) produces diagrams (VC8-1)-(VC8-14) (3–27).

In the same way the rest of the diagrams should be differentiated. Since the Fock operator depends upon occupied orbitals, F-rings on the diagrams (VC9)-(VC15) must also be differentiated. Diagram (VC9), after taking functional derivatives, produces diagrams (VC9-1)-(VC9-10) (3–28).
Diagram (VC10) produces diagrams (VC10-1)-(VC10-10) (3–29).

Diagram (VC11), produces diagrams (VC11-1)-(VC11-16) (3–30).
In the same way diagram (VC12) generates diagrams (VC12-1)-(VC12-16) of set (3–31)

Differentiation of diagram (VC13) gives us diagrams (VC13-1)-(VC13-15) (3–32)
After taking the functional derivative of diagram (VC14), we obtain diagrams (VC14-1)-(VC14-15) (3–33)

The last set of diagrams (VC15-1)-(VC15-15) can be produced by differentiation of diagram (VC15) (3–34)

Together with diagrams (V1)-(V6), all diagrams presented in this section form a set, which is necessary to construct the correlation kernel. The interpretation of all diagrams is given in Appendix A.
3.3 Properties of the Correlation Kernel

The second-order correlation kernel has different spin components, which can be represented by the formula

\[
\begin{align*}
    f_{\alpha\alpha}^{(n)}(r_1, r_2) &= \int dr_3 \int dr_6 X^{-1}_\alpha(r_1, r_3) h_{\alpha\alpha}(r_3, r_6) X^{-1}_\alpha(r_6, r_2) \\
    f_{\alpha\beta}^{(n)}(r_1, r_2) &= \int dr_3 \int dr_6 X^{-1}_\alpha(r_1, r_3) h_{\alpha\beta}(r_3, r_6) X^{-1}_\beta(r_6, r_2)
\end{align*}
\]  

(3–35)

Diagrams, which contain only one contour cannot produce \( h_{\alpha\beta} \) components after differentiation. Three of the diagrams (VC5)-(VC8) after differentiation can produce only diagrams contributing to the \( h_{\alpha\alpha} \) or \( h_{\beta\beta} \) parts. The diagrams (VC9-1)-(VC9-7), (VC9-9), (VC9-10), (VC10-1)-(VC10-7), (VC10-9), (VC10-10), (VC11-1)-(VC11-10), (VC11-13)-(VC11-16), (VC12-1)-(VC12-10), (VC12-13)-(VC12-16), (VC13-1)-(VC13-12), (VC13-14), (VC13-15), (VC14-1)-(VC14-12), (VC14-14), (VC14-15) have the same property. Diagrams containing 2 or more contours can produce all spin components. Sets of diagrams (VC1-7)-(VC1-16), (VC2-7)-(VC2-16), (VC3-7)-(VC3-14), (VC4-7)-(VC414), (VC15-7)-(VC15-12) have two contours, but both \( \hat{\delta} \)-functions present in one of the contours means that these diagrams make a contribution to \( h_{\alpha\alpha} \) or \( h_{\beta\beta} \) parts, but have an extra factor of 2. That factor appears after summation over all spin-orbitals of the second contour. Diagrams (VC1-1)-(VC1-6), (VC2-1)-(VC2-6), (VC3-1)-(VC3-6), (VC4-1)-(VC4-6), (VC9-8), (VC10-8), (VC11-11), (VC11-12), (VC12-11), (VC12-12), (VC13-13), (VC14-13), (VC15-1)-(VC15-6), (VC15-4)-(VC15-15) have \( \hat{\delta} \) functions on different contours, so they contribute to both \( h_{\alpha\alpha} \) and \( h_{\beta\beta} \) parts. Diagram (VC15-13) have an additional factor of 2 and also contribute into both spin parts. To build all spin parts of the correlation kernel we need to substitute the above diagrams into equation (3–35).

The next essential property of the exchange and correlation kernels is the symmetry with respect to permutation of its arguments

\[
f_{xc}^{(2)}(r_1, r_2) = f_{xc}^{(2)}(r_2, r_1)
\]  

(3–36)
This is possible because of equation (3–35) and

\[ h(r_1, r_2) = h(r_2, r_1) \quad (3–37) \]

To establish equation (3–35) we again need to analyze the structure of the diagrams. Diagrams (VC1-2), (VC1-5), (VC1-7), (VC2-1), (VC2-6), (VC2-7), (VC5-2), (VC5-7), (VC5-9), (VC6-2), (VC6-7), (VC6-9), (VC11-6), (VC12-6), (VC13-14), (VC14-15), (VC15-13), (VC15-11), (VC15-12), (V5) and (V6) are symmetric with respect to the permutation of variables \( r_1 \) and \( r_2 \). After consideration of the rest of the diagrams, it is easy to see that for each diagram there is another diagram, which differs from the initial one by only the interchanged variables, \( r_1 \) and \( r_2 \). Such pairs provide invariance with respect to permutation of variables.

During the construction of the correlation kernel Kohn-Sham (KS) orbitals and orbital energies are used. This implies the fact that our zero-order hamiltonian is chosen to be the Kohn-Sham choice

\[ H_0 = \sum_p \varepsilon_p \{ a_p^+ a_p \} \quad (3–38) \]

In all the diagrams containing the diagonal Fock matrix elements, \( f_{pp} \), should be replaced by \( f_{pp} - \varepsilon_p \) because all the matrix elements of the Kohn-Sham operator equal to zero, except the diagonal ones.

Like an exchange-correlation potential, the kernel is a local, multiplicative operator. This gives the possibility to use auxiliary basis sets for decomposition of kernels, what can be very helpful for implementation.

### 3.4 Numerical Testing

To calculate excitation energies the TDDFT equation (1–65) should be solved. In the adiabatic approximation it has the RPA-like form. The critical new quantity is the exchange-correlation kernel, \( f_{\sigma\tau}^{(xc)} \), which can be seen from the foregoing is a quite complicated quantity if we insist upon obtaining it rigorously for OEP-MBPT(2). The diagonal dependence of \( A \) on \( \epsilon_a - \epsilon_i \) tells us that if we are to get good excitation energies,
this zeroth-order difference should be a decent approximation to the excitation energy, and is, as shown elsewhere [16] when accurate exchange-correlation potentials are used. In this sense, the orbital energies in KS-DFT should have a certain meaning.

Furthermore, as pointed out in ref [16], we can also consider this equation to offer a Koopmans-like approximation to the principal ionization potentials, since, barring pathological behavior, when we allow an electron to be excited into the continuum, its orbital $a$ will then have no overlap with the bound orbital matrix elements of $h_{KS}$ and the kernel. Consequently, we are left with nothing but $-\epsilon_i$ in the TDDFT equations. So in this 'sudden', adiabatic approximation, the KS orbital energies should offer an estimate for each of the principal Ip’s, not just the highest-occupied (homo) one. When based upon the relatively correct $V_{xc}$ obtained from ab initio dft[16, 17] this estimate is superior to Koopmans’ theorem for the homo and the first few valence Ip’s, but is inferior for the core orbitals[26]. See also Chong, et al [25]. However, the OEP2 semi-canonical (sc) ab initio dft [16, 17] approximation has the distinct advantage that it uses a much better behaved unperturbed Hamiltonian than the usual KS choice, $H_0 = \sum_i h_{KS}(i)$.

To illustrate the evaluation of the kernel and the solution of TDDFT equations, we consider the Ne atom. All the excited states in Ne correspond to Rydberg excited states. To obtain reasonable values requires a quite extensive, diffuse basis set. We choose to start with the ROOS-ATZP atomic natural orbital basis[27] consisting of (14s9p4d1f) primitive gaussian functions contracted to a [5s4p3d1f] set. This underlying basis was then augmented by a set of even-tempered diffuse functions [3s3p3d], with exponential parameters $\xi = ab^n, a_s = 0.015, a_p = 0.013, a_d = 0.012, b=1/3$. The auxiliary basis is chosen to be the same, but without the $p$ and $d$ diffuse functions, since for the description of the exchange-correlation potential, diffuse functions are not necessary. The orbital energy estimates are shown in Table 3-1.

The ionization potential equation of motion coupled-cluster (IP-EOM CC) result in this basis for the Ne homo Ip is 21.3 eV with the experimental value being 21.5645
Table 3-1. Orbital energies and zero-order approximations to excitation energies

<table>
<thead>
<tr>
<th>orbital</th>
<th>IP[^{28}] Orbital (\varepsilon_a - \varepsilon_{HOMO})</th>
<th>Exchange-only Orbital (\varepsilon_a - \varepsilon_{HOMO})</th>
<th>OEP-MBPT(2) Excitation energies(exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>48.42</td>
<td>-46.19</td>
<td>-43.25</td>
</tr>
<tr>
<td>2p</td>
<td>21.56</td>
<td>-22.51</td>
<td>-20.23</td>
</tr>
<tr>
<td>3s</td>
<td>-5.15</td>
<td>17.36</td>
<td>-7.58</td>
</tr>
<tr>
<td>3p</td>
<td>-2.59</td>
<td>19.92</td>
<td>-3.72</td>
</tr>
<tr>
<td>4s</td>
<td>-1.95</td>
<td>20.56</td>
<td>-2.66</td>
</tr>
<tr>
<td>3d</td>
<td>-1.49</td>
<td>21.02</td>
<td>-2.05</td>
</tr>
</tbody>
</table>

\[^{28}\]. This compares to the OEPx value of 22.51 and OEP-MBPT(2) value of 20.23. The remaining unoccupied, but negative energy 3s orbital is changed by over 2 eV due to the MBPT(2) correlation. The OEP2(sc) \textit{ab initio dft} value changes this to 5.18 eV, attesting to the poor convergence of the standard KS partitioning of the Hamiltonian. Once OEP2(sc) calculations are done for the 3p, 4s, and 3d states, there is similar agreement between the OEPx and OEP2(sc) results, contrary to those shown in Table 3-2 for the standard (ks) choice.

Table 3-2. Excitation energies of Ne atom using OEP-MBPT(2) Kohn-Sham orbital energies

<table>
<thead>
<tr>
<th>Term</th>
<th>EOM-CCSD</th>
<th>TDDFT-exchange-only</th>
<th>TDDFT OEP-MBPT(2)</th>
<th>Exp[^{29}].</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^3)P</td>
<td>16.5353</td>
<td>17.1748</td>
<td>15.2132</td>
<td></td>
</tr>
<tr>
<td>(^1)P</td>
<td>16.7274</td>
<td>17.5209</td>
<td>11.4434</td>
<td>16.847</td>
</tr>
<tr>
<td>(^3)D</td>
<td>18.8303</td>
<td>19.8681</td>
<td>16.3320</td>
<td></td>
</tr>
<tr>
<td>(^1)D</td>
<td>18.8822</td>
<td>19.9181</td>
<td>16.9465</td>
<td>18.703</td>
</tr>
<tr>
<td>(^3)P</td>
<td>18.9156</td>
<td>19.9134</td>
<td>17.5645</td>
<td></td>
</tr>
<tr>
<td>(^1)P</td>
<td>18.9791</td>
<td>19.9134</td>
<td>17.7686</td>
<td>18.725</td>
</tr>
<tr>
<td>(^3)S</td>
<td>19.5118</td>
<td>19.8811</td>
<td>17.8663</td>
<td></td>
</tr>
<tr>
<td>(^1)S</td>
<td>19.9323</td>
<td>20.2983</td>
<td>17.3454</td>
<td>18.965</td>
</tr>
<tr>
<td>(^3)P</td>
<td>20.3747</td>
<td>20.4905</td>
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<tr>
<td>(^1)P</td>
<td>20.5588</td>
<td>20.6090</td>
<td>18.8788</td>
<td></td>
</tr>
</tbody>
</table>

Despite the differences, at least both the exchange-only and the OEP-MBPT(2) give qualitatively correct results for the Rydberg series. Helping to ensure this is the fact that the exchange potential has the correct asymptotic behavior and the exact cancellation
of self-interaction is assured. The correct asymptotic behavior is achieved using the Colle-Nesbet algorithm[30].

When we solve the TDDFT equations with the kernel developed in this paper, we obtain the results for excitation energies shown in Table 3-2. In general, just as we observed from the orbital energy differences, the OEP-MBPT(2) results tend to fall on the low side of experiment and the OEPx on the high side. In fact, except for the excitation energy for the lowest $^1P$ state, where the very low orbital energy of -7.58 biases the results, an average of the two would seem to be about right. There are, however, still differences in the basis set, as seen by the EOM-CCSD results compared to experiment, where besides the additional correlation effects introduced by EOM-CCSDT[31], the further extension of the diffuse functions would remove the ~1 eV error in the highest lying ($^1S$) state. Of course, the dependence of TDDFT on the basis and that for a two-particle theory like EOM-CC should be quite different.

The great sensitivity of the results to the orbital energies from the underlying KS-DFT calculation can be further appreciated by simply taking the energies from the OEPx results and using them in the evaluation of the kernel and the matrix elements in the TDDFT equations. These results are shown in Table 3-3. The near coincidence of results for OEPx and OEP-MBPT(2) is apparent, with both now being too high.

A similar experiment can be made where we use orbitals and orbital energies from OEP2(sc) ab initio dft results as described elsewhere[16], to obtain the results in Table 3-4. That is the TDDFT equations and the kernel are assumed to be the same, but we use orbitals and orbital energies obtained from OEP2(sc). Here we also show the results from standard TDDFT applications using the LDA and B3LYP functionals for comparison purposes. Clearly, we have improved results at both the OEPx(sc) and OEP2(sc) levels, with the same pattern of the former being too high, but less so; and the latter, too low, but better than before. It is apparent that the proper way to achieve the benefits of
OEP2(sc) is to develop TDDFT from the same principles, which will be pursued in future work.

### Table 3-3. Excitation energies of Ne atom using exchange-only orbital energies

<table>
<thead>
<tr>
<th>Term</th>
<th>TDDFT-exchange-only</th>
<th>TDDFT OEP-MBPT(2)</th>
<th>Exp[29]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{P}$</td>
<td>17.1748</td>
<td>17.0438</td>
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<tr>
<td>$^1\text{P}$</td>
<td>17.5209</td>
<td>17.1225</td>
<td>16.847</td>
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<td>$^1\text{D}$</td>
<td>19.9181</td>
<td>19.9262</td>
<td>18.703</td>
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<td>$^3\text{P}$</td>
<td>19.9134</td>
<td>19.9134</td>
<td>18.725</td>
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<td>$^1\text{P}$</td>
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<td>19.9134</td>
<td>18.725</td>
</tr>
<tr>
<td>$^3\text{S}$</td>
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<td>$^1\text{S}$</td>
<td>20.2983</td>
<td>21.3050</td>
<td>18.965</td>
</tr>
<tr>
<td>$^3\text{P}$</td>
<td>20.4905</td>
<td>20.4504</td>
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<tr>
<td>$^1\text{P}$</td>
<td>20.6090</td>
<td>20.4672</td>
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</tbody>
</table>

### Table 3-4. Excitation energies of Ne atom using orbital energies and orbitals from OEP2(sc). All equations for TDDFT are the same

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>$^3\text{P}$</td>
<td>16.5353</td>
<td>10.2805</td>
<td>13.3302</td>
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<td>13.3512</td>
<td>17.23</td>
<td>15.09</td>
<td>16.847</td>
</tr>
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<td>$^3\text{D}$</td>
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<td>14.8961</td>
<td>13.5076</td>
<td>19.74</td>
<td>17.56</td>
<td></td>
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<tr>
<td>$^1\text{D}$</td>
<td>18.8822</td>
<td>14.8949</td>
<td>13.5067</td>
<td>19.74</td>
<td>17.56</td>
<td>18.703</td>
</tr>
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<td>$^3\text{P}$</td>
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<td>17.56</td>
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<td>$^1\text{P}$</td>
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<td>14.4328</td>
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<td>18.725</td>
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<td>13.5077</td>
<td>19.74</td>
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</tr>
<tr>
<td>$^1\text{S}$</td>
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<td>13.9609</td>
<td>13.5057</td>
<td>19.74</td>
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<td>18.965</td>
</tr>
<tr>
<td>$^3\text{P}$</td>
<td>20.3747</td>
<td>15.0672</td>
<td>13.5077</td>
<td>20.40</td>
<td>18.29</td>
<td></td>
</tr>
<tr>
<td>$^1\text{P}$</td>
<td>20.5588</td>
<td>15.0712</td>
<td>13.5431</td>
<td>20.40</td>
<td>18.29</td>
<td></td>
</tr>
</tbody>
</table>

The cornerstone of OEP(sc) for exchange-correlation potentials is that we can impose the condition that the KS determinant has to give the exact, correlated density. Then this density condition provides equations that define $V_{xc}$ for a given functional[17]. Since no energy variational condition or functional derivative is used, we can change the choice of $H_0$ from the KS one to the semi-canonical (sc) one that offers greatly enhanced convergence of perturbation theory. But then there is no apparent immediate correspondence to a functional derivative as there is in the standard KS theory. A similar
condition to the density condition that would naturally lead to the analog of the kernel is necessary to correctly use the OEP2(sc) method. Of course, in infinite order methods, as opposed to perturbative approximations, there can be no difference between the two approaches.

3.5 Conclusions

The TDDFT kernel for an OEP method that includes a second-order MBPT(2) orbital-dependent correlation functional is derived. This derivation is made possible by a diagrammatic technique familiar from many-body theory. The complexity of the kernel for MBPT(2) is excessive, resulting in more than 200 diagrams that have to be evaluated. This is the price paid to retain the one-particle structure of DFT and TDDFT, yet introduce rigorous, orbital-dependent correlation functionals even at second order.

Yet, despite the kernel’s complexity it has been evaluated in a large basis set and illustrated for Ne. As only the KS choice of $H_0$ leads naturally to the kernel as the second functional derivative of the orbital-dependent functional, $E_{xc}$, the numerical result can suffer from the fact that the functional $E^{(0)} + E^{(1)} + E^{(2)}$ is not bounded, and without modification of $H_0$ as used in [16, 17, 26], the radius of convergence is poor, causing poor convergence[16] in determining the correlation potential. Nevertheless, the first step in the underlying framework has now been defined to apply TDDFT with OEP correlation potentials.

However, the complexity is great, though imposition of additional rigorous conditions might result in simplification of the kernel. Lacking such simplifications, the question arises as whether this is a case of diminishing returns to evaluate some 203 diagrams to retain the attractive, one-particle, correlated structure of DFT? First, the answers for Ne are not very good at the OEP-MBPT(2) level. Furthermore, the basis set dependence of OEP methods when done in gaussian basis is severe to even get the $V_{xc}$ right[16]. The failure of most such OEP calculations to satisfy the exact HOMO condition $<HOMO|K|HOMO> = <HOMO|V_{xc}|HOMO>$ is a case in point[16, 26].
Finally, there is no doubt that the standard equation of motion coupled-cluster methods (EOM-CC\cite{31}) are *less* time-consuming than is the present calculation. As long as the kernel for a rigorous orbital-dependent correlation potential is this complicated, two-particle wave function theories like EOM-CC are both superior and easier to do. But before we can further exploit the interface between DFT and wave function theory to the benefit of both, it is requisite to have the orbital-dependent kernel defined. This, and its initial evaluation, is what this chapter offers.
Consider a one-particle density operator in second-quantized form
\[ \hat{\rho}(r) = \sum_{p,q} \langle \varphi_p | \delta(r-r_1) | \varphi_q \rangle a_p^+ a_q \] (4-1)

Using Wick theorem, we rewrite this operator in normal form with the Kohn-Sham determinant as the Fermi-vacuum:
\[ \rho(r) = \sum_{p,q} \langle \varphi_p | \delta(r-r_1) | \varphi_q \rangle \{ a_p^+ a_q \} + \langle \Phi_{KS} | \delta(r-r_1) | \Phi_{KS} \rangle \]
\[ = \sum_{p,q} \langle \varphi_p | \delta(r-r_1) | \varphi_q \rangle \{ a_p^+ a_q \} + \sum_{i=1}^{N_{occ}} |\varphi_i(r)|^2 \] (4-2)

The second term is \( \rho_{ks} \), hence, the first term will be called the \textit{density correction}:
\[ \Delta \rho(r) = \sum_{p,q} \langle \varphi_p | \delta(r-r_1) | \varphi_q \rangle \{ a_p^+ a_q \} \] (4-3)

Since the converged Kohn-Sham scheme gives an exact density, all corrections to this density must be equal to zero. Hence, if we construct an effective operator of the density using MBPT, the correction to the density must vanish in any order\[17, 24\]. The first and second orders of the MBPT density condition can be written in the following way
\[ < \Phi_{KS} | (\Omega^{(1)+} + \Omega^{(2)+}) \Delta \rho(r) (\Omega^{(1)} + \Omega^{(2)}) | \Phi_{KS} >= \]
\[ = (\Omega^{(1)+} \Delta \rho(r))_{SC} + (\Delta \rho(r) \Omega^{(1)})_{SC} = 0 \] (4-4)

\[ < \Phi_{KS} | (\Omega^{(1)+} + \Omega^{(2)+}) \Delta \rho(r) (\Omega^{(1)} + \Omega^{(2)}) | \Phi_{KS} >= \]
\[ = (\Omega^{(1)+} \Delta \rho(r))_{SC} + (\Delta \rho(r) \Omega^{(1)})_{SC} + \]
\[ + (\Omega^{(2)+} \Delta \rho(r))_{SC} + (\Delta \rho(r) \Omega^{(2)})_{SC} + (\Omega^{(1)+} \Delta \rho(r) \Omega^{(1)})_{SC} = 0 \] (4-5)

Using the KS partitioning of the hamiltonian\[13\] and taking into account the relation \( f_{pq} = \varepsilon_p \delta_{pq} + \langle \varphi_p | V_x^{HF} - V_x(\rho) - V_c | \varphi_q \rangle \), it is possible to derive the same expressions for
the exchange and correlation potentials as a functional derivative of $E_x + E^{(2)}$ [13, 33]. However, this is a numerically hopeless procedure without any resummation of terms: (1) it suffers from adding a large diagonal term into the perturbation; (2) MBPT(2) is not bounded from below and any effort to use the variational condition $\frac{\delta E^{(2)}}{\delta \rho}$ is likely to suffer from numerical problems.

Our approach is to correct the above by changing the choice of $H_0$ and focusing on the expectation of the density operator instead of any variational functional derivation. The partitioning of the hamiltonian is chosen to be the one-body part as the zeroth-order approximation

$$H_0 = \sum_{\sigma} \sum_i f_{ii\sigma} \{a_{i\sigma}^+ a_{i\sigma}\} + \sum_b f_{bb\sigma} \{a_{b\sigma}^+ a_{b\sigma}\} + \sum_{i \neq j} f_{ij\sigma} \{a_{i\sigma}^+ a_{j\sigma}\} + \sum_{a \neq b} f_{ab\sigma} \{a_{a\sigma}^+ a_{b\sigma}\}$$

(4–6)

However, to avoid dealing with non-diagonal $H_0$, a semi-canonical transformation will be performed to obtain the more convenient zeroth-order hamiltonian,

$$H_0 = \sum_{\sigma} \sum_p \tilde{f}_{pp\sigma} \{\tilde{a}_{p\sigma}^+ \tilde{a}_{p\sigma}\}$$

(4–7)

Dropping the $\sim$ for simplicity, with the semi-canonical partitioning of the hamiltonian the OEP exchange and correlation potentials assume the following form

$$V_{x\sigma}(r) = -2 \int dr_1 \sum_{i,j,a} \frac{i_{i\sigma} j_{j\sigma} a_{a\sigma} > \varphi_{i\sigma}(r_1) \varphi_{a\sigma}(r_1)}{f_{ii\sigma} - f_{a\sigma a\sigma}} X_{\sigma}^{-1}(r, r_1)$$

(4–8)

$$V_{c\sigma}(r) = \int dr_1 (2 \sum_\tau \sum_{i,j,a,b,c} \frac{i_{i\sigma} j_{j\sigma} a_{a\sigma} b_{\tau} > - \varphi_{i\sigma}(r_1) \varphi_{a\sigma}(r_1)}{(f_{ii\sigma} + f_{jj\tau} - f_{a\sigma a\sigma} - f_{bb\tau})(f_{ii\sigma} - f_{cc\sigma})}$$

$$-2 \sum_\tau \sum_{i,j,k,a,b} \frac{i_{i\sigma} j_{j\sigma} k_{k\sigma} b_{\tau} > - \varphi_{i\sigma}(r_1) \varphi_{a\sigma}(r_1)}{(f_{ii\sigma} + f_{jj\tau} - f_{a\sigma a\sigma} - f_{bb\tau})(f_{kk\sigma} - f_{aa\sigma})}$$

$$- \sum_\tau \sum_{i,j,k,a,b} \frac{i_{i\sigma} j_{j\sigma} k_{k\sigma} l_{l\sigma} > - \varphi_{i\sigma}(r_1) \varphi_{a\sigma}(r_1)}{(f_{ii\sigma} + f_{jj\tau} - f_{a\sigma a\sigma} - f_{bb\tau})(f_{kk\sigma} + f_{ll\tau} - f_{aa\sigma} - f_{bb\tau})}$$
\[
\begin{align*}
&+ \sum_{\tau} \sum_{i,j,a,b,c} \text{<} \sigma \text{,} \tau \text{>} \text{<} \text{c_i} \text{a}_\sigma \text{b}_\tau \text{>} - \text{<} \text{c_j} \text{a}_\sigma \text{b}_\tau \text{>} \text{<} \text{c_i} \text{a}_\sigma \text{b}_\tau \text{>} \\
&\quad \times (f_{iis} + f_{jjs} - f_{ais} - f_{bbs}) (f_{iis} + f_{jjs} - f_{cis} - f_{bbs}) \\
&+ \sum_{a,b,i} f_{iba} f_{iia} \Phi_{ia}(r_1) \Phi_{ia}(r_1) (f_{iis} - f_{ais}) (f_{iis} - f_{ais}) (f_{jja} - f_{bbs}) \\
&+ \sum_{a,b,i} f_{iaa} f_{ibb} \Phi_{ia}(r_1) \Phi_{ia}(r_1) (f_{jja} - f_{bbs}) (f_{jja} - f_{bbs}) \\
&- \sum_{i,j,a,b} f_{bja} (\text{<} a_i \sigma \text{b} j_{\sigma} \text{>} + \text{<} a_i \sigma \text{b} j_{\sigma} \text{>}) \Phi_{ia}(r_1) \Phi_{ia}(r_1) \Phi_{ia}(r_1) \Phi_{ia}(r_1) \Phi_{ia}(r_1) \Phi_{ia}(r_1) \\
&\quad \times X^{-1}(r_1, r)
\end{align*}
\]

(4-9)

where

\[
X_{\sigma}(r_1, r) = 2 \sum_{a,i} \frac{\Phi_{ia}(r_1) \Phi_{ia}(r_1) \Phi_{ia}(r_1) \Phi_{ia}(r_1) \Phi_{ia}(r_1) \Phi_{ia}(r_1)}{f_{iis} - f_{ais}}
\]

(4-10)

Exchange and correlation potentials, given by equations (8) and (9) must be substituted into the Kohn-Sham equations on each iteration, until the fully self-consistent solution is obtained. The method is implemented, using gaussian basis sets for orbitals and exchange-correlation potentials as described in references [13, 17].

4.2 Results and Discussion

4.2.1 Total Energies

Ground-state energies are calculated for several systems with results presented in Table 4-1. The uncontracted ROOS-ATZP basis is used for the Ne atom, while the rest of the atoms and molecules are calculated using the uncontracted ROOS-ADZP basis[27]. All the molecules and their ions are considered to be in the equilibrium geometry[36] of the corresponding neutral system, except when potential energy curves are considered.

For \textit{ab initio} DFT calculations exchange-correlation potentials are used from [13] and equations (4–8)–(4–9). For the comparison energies obtained from KS DFT with the Perdew- Burke-Ernzerhof[34] (PBE) exchange-correlation potential and coupled-cluster with single, doubles and perturbative triple excitation[35] (CCSD(T)) are also shown in Table 4-1. Total energies, calculated with OEP-MBPT(2), based on the density condition approach with the semi-canonical partitioning are much closer to CCSD(T) then OEP-MBPT(2) with the KS partitioning. The latter greatly overestimates correlation energy.
and frequently diverges. Since the density condition approach is completely equivalent to the variational OEP-MBPT(2) for the KS partitioning it has the same problems. However, in the case of the non-variational, semi-canonical density condition approach, the unboundness from below is less of a problem. The semi-canonical choice of \( H_0 \) provides good approximations to the energy and wave function in MBPT(2) and the corresponding total energies are much closer to highly-accurate CCSD(T) ones, at least in the chosen basis. The computational cost of the OEP-MBPT(2) method is comparable with the cost of MBPT(2), the scaling of both methods is \( N^5 \), where \( N \) is the number of basis functions. This is more expensive than conventional DFT (scales like \( N^3 \)), but less expensive then CCSD(T), computational time of which is proportional to \( N^7 \). The correlation potential, calculated with the semi-canonical OEP for the Ne atom[16] is close to the corresponding quantum Monte-Carlo potential, and we can expect that for other systems, where QMC is not available, semi-canonical OEP-MBPT(2) potentials should be a good alternative. For the open-shell case potentials produced by Kohn-Sham OEP show an overestimation of the correlation energy, the same situation previously reported for the closed-shell case[16]. (Fig 4-1 and 4-2). The correct \(-\frac{1}{7}\) long-range asymptotic behavior of the OEP-MBPT(2)

<table>
<thead>
<tr>
<th></th>
<th>MP2</th>
<th>OEP-KS</th>
<th>OEP-semi</th>
<th>PBE</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2^+ )</td>
<td>-108.886335</td>
<td>no conv</td>
<td>-108.905444</td>
<td>-108.890773</td>
<td>-108.900556</td>
</tr>
<tr>
<td>( N )</td>
<td>-54.544740</td>
<td>-54.593111</td>
<td>-54.545199</td>
<td>-54.535569</td>
<td>-54.564854</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>-76.370003</td>
<td>-76.510744</td>
<td>-76.373092</td>
<td>-76.369991</td>
<td>-76.383576</td>
</tr>
<tr>
<td>( H_2O^+ )</td>
<td>-75.901155</td>
<td>-75.989525</td>
<td>-75.902958</td>
<td>-75.912146</td>
<td>-75.921765</td>
</tr>
<tr>
<td>( CN )</td>
<td>-92.598196</td>
<td>no conv</td>
<td>-92.651919</td>
<td>-92.646898</td>
<td>-92.658287</td>
</tr>
<tr>
<td>( CN^- )</td>
<td>-92.772714</td>
<td>no conv</td>
<td>-92.780718</td>
<td>-92.783715</td>
<td>-92.796498</td>
</tr>
<tr>
<td>( CO )</td>
<td>-113.228520</td>
<td>-113.511203</td>
<td>-113.237817</td>
<td>-113.239593</td>
<td>-113.251239</td>
</tr>
<tr>
<td>( CO^+ )</td>
<td>-112.702208</td>
<td>no conv</td>
<td>-112.734813</td>
<td>-112.729947</td>
<td>-112.739892</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>-150.205776</td>
<td>no conv</td>
<td>-150.222180</td>
<td>-150.255051</td>
<td>-150.221560</td>
</tr>
<tr>
<td>( Ne )</td>
<td>-128.859589</td>
<td>-128.951437</td>
<td>-128.861175</td>
<td>-128.865844</td>
<td>-128.865133</td>
</tr>
<tr>
<td>( Ne^+ )</td>
<td>-128.066796</td>
<td>no conv</td>
<td>-128.067574</td>
<td>-128.068711</td>
<td>-128.080202</td>
</tr>
</tbody>
</table>

Mean error, kJ/mol: 58.22, 26.74, 36.16
exchange potentials (Fig 4-1 and 4-2) is guaranteed by the use of the Colle-Nesbet seed potential algorithm[30]. In all our calculations a Slater potential[38] was used as a seed potential, since the Colle-Nesbet algorithm requires the seed potential to be as close as possible to the actual potential. Two separate Slater potentials, one for alpha and the other for beta, were used. For all the closed-shell systems from Table 4-1, the numerical

Figure 4-1. Exchange and correlation potentials of Li atom (radial part). A) Exchange potential. B) Correlation potential

Figure 4-2. Exchange and correlation potentials of $O_2$ molecule across the molecular axis. A) Exchange potential. B) Correlation potential

results obtained from OEP-MBPT(2) with the semi-canonical potential and from DFT
with the PBE potential are numerically close, and close to the reference CCSD(T) energies. This, of course, is part of the power of GGA and meta DFT, even when such energies are obtained with highly erroneous potentials. Instead, PBE partly benefits from the cancellation of errors in $V_x$ and $V_c$ (Fig 1 and 2). For most of the open-shell systems the energies of the semi-canonical OEP-MBPT(2) are much closer to CCSD(T) then the corresponding PBE energies, which is also a consequence of the wrong behavior of the PBE potential.

4.2.2 Ionization Potentials

Orbital energies and the corresponding ionization potentials are much more sensitive to the exchange-correlation potential than the total energies. Vertical ionization potentials, calculated as energy differences between the neutral and its ionized system are calculated using the same basis sets and geometries as in the previous section. Results are presented in Table 4-2. In exact DFT, the energy of the highest occupied molecular

<table>
<thead>
<tr>
<th></th>
<th>HOMO, OEP-semi</th>
<th>$\Delta E$, OEP-semi</th>
<th>HOMO, PBE</th>
<th>$\Delta E$, PBE</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>21.01</td>
<td>21.59</td>
<td>13.35</td>
<td>21.69</td>
<td>21.56</td>
</tr>
<tr>
<td>$N_2$</td>
<td>16.89</td>
<td>15.03</td>
<td>10.27</td>
<td>15.41</td>
<td>15.58</td>
</tr>
<tr>
<td>CO</td>
<td>13.68</td>
<td>13.69</td>
<td>9.05</td>
<td>13.87</td>
<td>14.01</td>
</tr>
<tr>
<td>$CN^-$</td>
<td>4.19</td>
<td>3.51</td>
<td>0.149</td>
<td>3.72</td>
<td>3.86</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>12.37</td>
<td>12.73</td>
<td>7.08</td>
<td>12.46</td>
<td>12.62</td>
</tr>
<tr>
<td>N</td>
<td>15.25</td>
<td>14.52</td>
<td>8.30</td>
<td>14.73</td>
<td>14.53</td>
</tr>
<tr>
<td>Li</td>
<td>4.89</td>
<td>5.38</td>
<td>3.23</td>
<td>5.59</td>
<td>5.39</td>
</tr>
</tbody>
</table>

Table 4-2. Ionization potentials (in e. v.)

orbital (HOMO) corresponds to the negative of the exact vertical ionization potential. In the case of the semi-canonical OEP the HOMO energy is close to the corresponding $\Delta E$ values, what can be explained by the correct shape of the exchange-correlation potential (Fig 4-1 and 4-2 and ref [16, 17]), while PBE does not exhibit correct behavior of potential and thus, fails to reproduce the correct HOMO energy values. Failure to reproduce the correct HOMO energy causes the incorrect integer discontinuity of the PBE (or any other GGA) exchange-correlation potential[39, 40].
4.2.3 Dissociation Energies

Dissociation energies, calculated with semi-canonical OEP and PBE are presented in Table 4-3. Potential curves for the LiH, OH and HF molecules are shown on Fig 4-3, 4-4 and 4-5. For all curves the dissociation energies have approximately the same level of accuracy as in the MBPT(2) case, but the semi-canonical OEP-MBPT(2) improves the shape of the curves.

Table 4-3. Dissociation energies (in kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>OEP-semi</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>1013.27</td>
<td>964.56</td>
<td>941.64</td>
</tr>
<tr>
<td>O₂</td>
<td>598.14</td>
<td>549.12</td>
<td>493.59</td>
</tr>
<tr>
<td>CO</td>
<td>1122.16</td>
<td>1122.00</td>
<td>1071.80</td>
</tr>
<tr>
<td>CN</td>
<td>821.151</td>
<td>794.51</td>
<td>745.01</td>
</tr>
</tbody>
</table>

4.2.4 Singlet-Triplet Separation in Methylene

Results for the extensivly studied splitting of singlet and triplet states of methylene [41, 42] are reported, using the uncontracted ROOS-ADZP basis sets: 13s9p3d for carbon and 8s4p1d for hydrogen. Equilibrium geometries for both states are taken from reference [41]. The energies for the two states, calculated with different methods are presented in Table 4-4. There are significant differences in the energy separation compared to the experimental value (8.998 kcal/mol) for all of the presented methods. This is a basis set issue, but can also be explained by the fact that the singlet state of methylene has a significant contribution from two-determinants[41], so MBPT(2) is a much poorer underlying approximation for their difference than infinite-order CCSD or CCSD(T), and especially the two-determinant CCSD (TD-CCSD) results[41]. Where the absolute values of PBE energies are not too good for the two states of \( CH₂ \), the difference is consistent with MBPT(2) and its OEP-generated \textit{ab initio dft} form.

4.3 Conclusions

\textit{Ab initio dft} calculations with OEP-MBPT(2) semi-canonical potentials show significantly improved results over OEP-MBPT(2) with the Kohn-Sham partitioning of
Table 4-4. Singlet and triplet energies of methylene

<table>
<thead>
<tr>
<th>Method</th>
<th>$^3B_1$</th>
<th>$^1A_1$</th>
<th>$\Delta E$, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T)</td>
<td>-39.127004</td>
<td>-39.109751</td>
<td>10.826</td>
</tr>
</tbody>
</table>

$H_0$. In all cases, when the Kohn-Sham partitioning scheme fails to converge, the semi-canonical version had no problem with convergence. The corresponding HOMO energies are close to the correct ionization potentials for neutral systems and electron affinities for anions, and they correct the integer discontinuity of standard exchange-correlation potentials. In the case of open-shell systems, semi-canonical OEP-MBPT(2) also shows improvement in total energies over PBE results and produce more accurate atomization energies. Finally, correlation potentials, produced by the semi-canonical OEP-MBPT(2) method, can be used as the first of a sequence of highly correlated methods that provides a reference for the construction of density-dependent functionals.
Figure 4-3. LiH potential energy curve.
Figure 4-4. OH potential energy curve.
Figure 4-5. HF potential energy curve.
Kohn-Sham (KS) density functional theory\[5, 6\] (DFT) is a widely used method for ground-state energies and other properties. The time- dependent extension of Kohn-Sham DFT, whose rigorous foundation has been questioned \[43\], is a very popular method for the description of excited states energies, since it can often provide accurate results by the diagonalization of a single-excitation dimensional matrix as in time-dependent Hartree-Fock or mono-excited CI. However KS DFT and TDDFT have their natural limitations. Standard functionals suffer from an incomplete cancellation of self-interaction terms in the KS equations and incorrect long-range asymptotic behavior of the potentials. Both can be particularly troublesome for excited, particularly Rydberg states, and ionized states\[16, 21, 48\], making it difficult to get systematically improvable results from standard TDDFT.

Exact-exchange density functional theory is based on the optimized effective potential method introduced by Talman and Shadwick\[15\]. In this method the exchange potential is defined as the functional derivative of the non-local orbital-dependent exchange functional from the Hartree-Fock method (EXX), ie \[\delta E_X / \delta \rho(1) = V_X(1)\]. The OEP method is free from the self-interaction problem, it exhibits the correct \[-\frac{1}{r}\] asymptotic behavior and its highest occupied molecular orbital (HOMO) energy satisfies Janak’s theorem\[44\]

\[
< h | \tilde{V}_x | h > = - < h | \tilde{K} | h >
\]  

(5–1)

where \(\tilde{K}\) is the non-local Hartree-Fock exchange operator. Recently the exchange-only OEP method has been formulated in several, not always consistent, or even formally correct ways\[16, 22, 45–47\], and these alternative approaches can suffer from numerical problems. However, when evaluated with a proper treatment of the density-density response matrix \(X\), most of the numerical problems that have been encountered are resolved.
Our preference in the development of such orbital dependent functionals and potentials is to start from the density condition that is fundamental to KS theory, as the single determinant must provide the correct density for the exchange-correlation problem. Once this is enforced for a given functional, \( V_{XC} \) is uniquely determined up to a constant. This is the origin of the perturbation method of Goerling and Levy\[14\], but essentially modified by Bartlett \textit{et al} \[16, 17\] to avoid the failures of a simple sum of KS one-particle Hamiltonians as the unperturbed problem, to generate \textit{correlation} potentials. This is the cornerstone of \textit{ab initio} DFT. The conceptual difference is that the density condition does not explicitly use the variational determination, \( \delta E_{XC}/\delta \rho(1) = V_{XC}(1) \). This difference is of critical importance in generating \textit{correlation} potentials from low-orders of perturbation theory. Without that change, no low-order orbital dependent correlation functional like that from MBPT2 will generally work, but with those changes, it does very well \[16, 48\]. Those modifications to the perturbation theory also pertain to the exchange-only case, the subject of this paper, but for that problem the distinctions are less important\[16\].

Once following this approach, which starts with the KS choice of \( H_0 \), the distinctions between applying the density condition and using direct functional differentiation is more conceptual than essential, as there is a correspondence in any order of perturbation theory\[24, 37\].

The direct optimization procedure advocated by some, built upon the above variational determination of the functional derivative, though formally equivalent, differs from the original, \textit{X}-based OEP in the details of implementation. However, as was pointed out by Staroverov \textit{et al} \[45\] under certain combinations of molecular and auxiliary basis sets, particularly when the latter’s dimension is larger than that for the former, the direct optimization method can give the Hartree-Fock energy and density. The latter can be viewed as a trivial solution, as it can be shown to correspond to the solution of a weighted least-squares expression. On the other hand, the \textit{X}-based OEP with proper handling is
quite stable, and does not suffer from the problems alluded to by Staroverov, et. al, even when the auxiliary basis has a dimension greater than the MO basis.

In another interesting example, Rohr, et al[49] observes the occurrence of a degeneracy in performing OEP calculations, and to investigate this, intentionally construct a problem where the HOMO and LUMO orbitals of the KS problem are degenerate. Subject to direct minimization, they proceed to report on the failure of the OEP procedure. On the other hand, it is shown in this paper that the original X based approach handles this problem, too.

The exchange-only time-dependent OEP has been considered by Goerling[20] and implemented by Hirata et. al[21, 50]. However, all results to date are for closed-shell systems. To further address the exact local (OEPx) exchange versus time-dependent Hartree-Fock (TDHF), TDOEPx is generalized to treat excited states for open-shell species. Results from adiabatic TDOEPx are in good agreement with TDHF for both excitation energies and polarizabilities, however, it is shown that charge-transfer states cannot be properly described in TDDFT. For standard DFT methods, gradient-corrected, hybrid, etc. this has been noted, and improved upon[51], but standard methods, unlike TDOEPx, still suffer from other limitations, like the self-interaction error and the incorrect long-range behavior of the potentials and kernels. In an approach that gives the ’right answer for the right reason’ these exact conditions are requisite. In TDOEPx there are no such errors. Hence, failures of TDOEPx compared to TDHF have to be exclusively due to the local versus non-local exchange operator, which is demonstrated.

Finally, $C_6$ coefficients are obtained for open-shell systems from the TDOEPx frequency-dependent polarizability.

5.1 Exact-Exchange Density Functional Theory

The most satisfactory way to introduce exact exchange DFT is to insist that the Kohn-Sham single determinant provide the exact density, but subject to a local, multiplicative exchange operator, $\hat{V}_X(1)$, instead of the usual non-local Hartree-Fock
\[
K(1) \phi_p(1) = \sum_j \int \phi_j^*(3) \frac{P_{13}}{r_{13}} \phi_j(3) d3 \phi_p(1) = \sum_j \int \phi_j^*(3) \frac{P_{13}}{r_{13}} \phi_p(3) d3 \phi_j(1)
\]

where the \( \{ \phi_j \} \) are the occupied Kohn-Sham spin orbitals, \( p=i,j,k,l,... \). The latter are the solutions to the equations,

\[
\hat{h}_S \phi_p(1) = \epsilon_p \phi_p(1) \quad (5-3)
\]

\[
\hat{h}_S(1) = \hat{h}(1) + \hat{J}(1) + \hat{V}_X(1)
\]

\[
\hat{J}(1) = \sum_j \int \phi_j^*(2) \frac{1}{r_{12}} \phi_j(2) d2
\]

\[
= \int \frac{\rho(1)}{r_{12}} d2 \quad (5-6)
\]

\[
\rho_{KS}(1) = \sum_j \phi_j^*(1) \phi_j(1) \quad (5-7)
\]

where the unoccupied orbitals are indicated by \( p=a,b,c,d,... \).

The condition that the density, \( \rho(1) \), be the Hartree-Fock one, is that

\[
f_{ia} = \langle \phi_i^{HF} | \hat{h} + \hat{J} - \hat{K} | \phi_a^{HF} \rangle = 0 \quad (5-8)
\]

\[
\rho_{HF}(1) = \sum_j \phi_j^{HF*}(1) \phi_j^{HF}(1) \quad (5-9)
\]

which, as is well-known, is correct through first order in correlation measured relative to the sum of HF one-particle operators, \( H_0 = \sum_i f(i) \), due to the Moeller-Plesset theorem.

For KS orbitals, \( f_{ia} \) is not zero. Hence, if the objective were to maximize the similarity in the KS and HF density, it would then require minimizing a quantity composed of KS orbitals, related to

\[
\min \sum_{i,a} |\langle i | \hat{f} - \hat{h}_S | a \rangle|^2 = \min \sum_{i,a} |\langle i | \hat{K} + \hat{V}_X | a \rangle|^2
\]

suggesting a kind of least-squares minimization as has been discussed previously[13, 16, 17, 48]. Clearly, this minimization would have the trivial solution that \( \langle i | K | a \rangle = -\langle i | V_X | a \rangle \).
However, there are some other pertinent considerations before doing so. The condition that the KS single determinant gives the exact density through first order in its correlation perturbation, obviously imposes the condition that $\rho_{KS}^{(1)} = 0$. This density condition is very general as it applies to exchange and correlation, and has been used quite successfully in defining \textit{ab initio} DFT exchange and, in higher orders, correlation potentials\cite{13, 16, 17, 48}, since it also transcends any particular separation of the Hamiltonian in perturbation theory. In particular, it is \textit{not} subject to $H_{KS}^{0} = \sum_{i} h_{S}(i)$, and thereby alleviates the pathological behavior that gives no convergence when defining such correlation potentials from MBPT(2), for example \cite{13}. For the exchange only, however, such effects are less important\cite{16, 17}. Therefore this paper will use the sum of Sham Hamiltonians, but the principle for derivation remains the same.

Hence, requiring that

$$0 = \rho_{KS}^{(1)} = \langle \Phi_{KS} | \hat{\Delta} R_{0} \hat{V} | \Phi_{KS} \rangle + \langle \Phi_{KS} | \hat{V} R_{0} \hat{\Delta} | \Phi_{KS} \rangle$$

(5-11)

$$\hat{\Delta} = \sum_{i} \hat{\rho}(x_{i} - x_{i}^{\prime})$$

(5-12)

$$R_{0} = \sum_{i,a} |a_{i}^{\prime} \rangle (\epsilon_{i} - \epsilon_{a})^{-1} |a_{i} \rangle + \sum_{l<j,a<b} |ab_{ij} \rangle (\epsilon_{i} + \epsilon_{j} - \epsilon_{a} - \epsilon_{b})^{-1} |ab_{ij} \rangle + ...$$

(5-13)

$$= \{|h_{1}\rangle R_{0}^{1} |h_{1}\rangle | + |h_{2}\rangle R_{0}^{2} |h_{2}\rangle | + ...$$

(5-14)

$$V = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i} \hat{J}(i) + \hat{V}_{X}(i)$$

(5-15)

Single excitations in the resolvent operator are indicated by $|a_{i}^{\prime}\rangle$, and collectively by the row matrix, $|h_{1}\rangle$, doubles by $|ab_{ij}\rangle$, $|h_{2}\rangle$, etc. It is easy to show\cite{17} that only the singles contribute to the first-order density, and

$$\rho_{KS}^{(1)} = \sum_{i,a} \langle i | \hat{\rho} | a \rangle f_{ia} \frac{1}{\epsilon_{i} - \epsilon_{a}} + cc = 2 \sum_{i,a} \phi_{i}^{*}(1) \phi_{a}(1) \langle i | \hat{K} + \hat{V}_{X} | a \rangle / (\epsilon_{i} - \epsilon_{a}) = 0$$

(5-16)

Then this condition defines the $\hat{V}_{X}(1)$ operator up to a constant\cite{52}. Note that this is a pointwise condition as it should equal zero at \textit{all} $x_{i}$, but actually imposes the weaker
condition, discussed in [52]. In addition to its pointwise character represented by the delta function, it differs from the above least-squares form by the presence of the denominator. The usual way to write the above equation is to introduce the non-interacting density-density response function,

\[ X(1, 2) = \sum_{i,a} \phi_i^*(1)\phi_a(1)\phi_a^*(2)\phi_i(2) / (\epsilon_i - \epsilon_a) \] (5–17)

which then gives

\[ \int X(1, 2)[\hat{K}(2) + \hat{V}_X(2)]d^2 = \sum_{i,a} \frac{\phi_i^*(1)\phi_a(1)}{\epsilon_i - \epsilon_a} \int \phi_a^*(2)[\hat{K}(2) + \hat{V}_X(2)]\phi_i(2)d^2 = 0 \forall x_1 \]

\[ = \sum_{i,a} w_{ia}(1) \int \phi_a^*(2)[\hat{K}(2) + \hat{V}_X(2)]\phi_i(2)d^2 = 0 \forall x \] (5–18)

This is the usual optimized-effective potential procedure of Talman and Shadwick[15, 22], geared toward representing the \( V_X \) operator on a numerical grid. The weight factor, \( w_{ia}(1) \), is also introduced. Note the matrix elements can be written in configuration space as

\[ (V_X)_{ai} = \langle a|\hat{V}_X|i \rangle \] (5–19)

\[ V_X = \langle h_1|\hat{V}_X|0 \rangle \] (5–20)

\[ (\hat{K})_{ai} = \sum_j \langle aj|ji \rangle \] (5–21)

\[ K = \langle h_1|\hat{K}|0 \rangle \] (5–22)

Also note that the response function can be written as

\[ X(1, 2) = \langle 0|\Delta|h_1 \rangle R_0^1\langle h_1|\Delta|0 \rangle = a_1 R_0^1 a_1^\dagger \leq 0 \] (5–23)

which makes the point that, for the ground state, \( X(1, 2) \) is semi-negative definite since \( R_0^1 \) is.
To make the transition from an infinite basis to a finite computational basis, one introduces the matrix representation of the OEP equation. Eqn (5–18) then becomes,

\[ \mathbf{w}(\mathbf{V}_X + \mathbf{K}) = 0 \]  
\[ \mathbf{w} = \mathbf{a}_1 \mathbf{R}_0^1 \]  

Using weighted least squares

\[ \delta \mathbf{V}_X \left[ \sum_{i,a} \omega_{ia} | < i | \mathbf{V}_X | a > + K_{ia}^2 \right] = 0 \]  

(5–26)

gives the OEP equation, Eqn (5–16).

As is customary in practice, the computational form for the OEP equation can be obtained by twice applying the one-electron projector,

\[ \mathbf{O}^{(1)} = | \eta > < \eta | \eta >^{-1} | \eta | \]

where \( | \eta \rangle \) defines an auxiliary basis, respectively, for electron 1 and 2. Without restriction the basis can be assumed to be orthonormal The so-called outer projection[53] of the response function is then

\[ \mathbf{X}_{\mu
u} = \sum_{i,a} \langle \mu a i \rangle \langle i a \nu \rangle / (\epsilon_i - \epsilon_a) \]  

(5–27)

Using this expression and insisting upon the linear independence of \( | \eta \rangle \) gives the OEP equations in the form,

\[ < \eta | \mathbf{X}(1, 2) | \eta > < \eta | \mathbf{V}_X (2) + \circ \mathbf{K} (2) > = 0 \forall x_1 \]  
\[ \mathbf{XV}_X = \mathbf{Y} \]  
\[ \mathbf{Y}_\mu = \sum_{i,a,j} \frac{\langle \mu a i \rangle}{(\epsilon_i - \epsilon_a)} \langle i j | j a \rangle \]  
\[ \mathbf{V}_X = \mathbf{X}^{-1} \mathbf{Y} \]  

(5–28)  
(5–29)  
(5–30)  
(5–31)

where the \( \circ \) indicates the product of \( \mathbf{X} \) and \( \mathbf{K} \) in Eqn (5–18) that results in the \( \mathbf{Y} \) column matrix.
In practice, the matrix $X$ is explicitly non-singular in a finite, linearly independent basis\textsuperscript{[52]}, unlike the infinite basis analogue of $X(1,2)$, which has to be singular\textsuperscript{[52, 54]}. The latter follows because the infinite basis cannot account for the arbitrary constant. However, in a finite basis, $X$ is ill-conditioned because the null-space of functions orthogonal to $V_X$ can always be added to $V_X$, but with zero weight, and this requires that the OEP equations produce a computed, numerical zero. This makes the equations difficult to invert, recommending a singular-value decomposition (SVD) procedure. This SVD should not be confused with the need to exclude linear dependency in the computational basis, which can always be achieved independently; but that, too, would be accommodated in practice by the SVD procedure.

The role of $X$ is to impose the point-wise closeness of $\hat{K}$ and $\hat{V}_X$, and, as such, it is critical to the determination of OEP potentials. In the absence of $X$, as attempted by Staroverov, et al.\textsuperscript{[45]} unphysical results can be obtained. According to their procedure \textsuperscript{[45]}, to get HF energies and densities from the OEP method (i.e. to find the trivial solution of Eqn(5–26)), the number of auxiliary functions used must be greater or equal to some number, $N_{\text{min}}$, which is the number of non-zero $K_{ia}$ matrix elements. In this case equation(8) of ref\textsuperscript{[45]} will have one or more solutions.

To illustrate, the use of the response matrix approach, we report in Figure 5-1 the results for the Ne atom exchange potentials using the three basis sets used by Staroverov, et al, plus a fourth uncontracted Roos basis that we prefer. The auxiliary bases are the same as the molecular ones and in all cases the number of auxiliary functions is larger than the corresponding $N_{\text{min}}$, necessary for the solution of equation (8) of ref \textsuperscript{[45]}. The total energy values from Table 5-1 and corresponding potentials from Fig 5-1 are completely opposite to the results of ref\textsuperscript{[45]} because of the broken pointwise closeness and the absence of the self-consistent solution. Note that once the pointwise closeness is imposed via X, and a self-consistent solution obtained, there is no problem for the proper SVD-based OEP procedure.
Inspired by an observation of Jiang[55] of HOMO and LUMO degeneracy arising in OEP, Rohr et al[49] offered a specific combination of molecular and auxiliary basis, that showed their effect for He, then using the direct optimization algorithm produces degenerate HOMO and LUMO orbital energies. We performed OEP calculation for the He atom using the optimized auxiliary basis from Table 1 of ref[49], which caused their degeneracy, but instead of using the direct minimization algorithm of Broyder-Fletcher-Goldfarb-Shanno (BFGS) the solution of the OEP equation is solved by the inversion of $X$ with the SVD procedure. These results are presented in Table 5-2, demonstrating that

Table 5-2. Total and orbital energies of He atom

<table>
<thead>
<tr>
<th></th>
<th>OEP</th>
<th>HF</th>
<th>OEP2-KS</th>
<th>OEP2-sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy, a. u.</td>
<td>-2.86115365</td>
<td>-2.86115365</td>
<td>-2.90524738</td>
<td>-2.89488588</td>
</tr>
<tr>
<td>LUMO energy, e. v.</td>
<td>3.591</td>
<td>15.561</td>
<td>3.671</td>
<td>3.618</td>
</tr>
</tbody>
</table>
the $X$ based OEP have no problem even for this situation.

As seen in Table 5-2, even the notoriously unstable second-order OEP procedure, based on $H_{0}^{KS}$ has no particular difficulties, either. Since the direct minimization procedure of Yang and Wu[46] is based on the same equation as the regular OEP method, all of the problems, described in ref [49], are caused by using the BFGS algorithm instead of solving the OEP Fredholm equation with the SVD procedure for the $X$. That might appear to be surprising since $\epsilon_{h} = \epsilon_{i}$, would mean that the resolvent operator is manifestly singular, clearly not that appropriate to a non-degenerate perturbation theory functional, which has always been the intent of such orbital dependent expressions. However, it is also apparent from the standard, chain-rule differentiation used by Rohr et al[49], namely

$$V_{XC}(1) = \delta E_{XC}/\delta \rho(1) = \sum_{p} \int \int d^{2}d^{3}[\delta E_{XC}/\delta \phi_{p}(2)][\delta \rho_{p}(2)/\delta v_{s}(3)][\delta v_{S}(3)/\delta \rho(1)]$$
(5–32)

that the derivative would not be defined from the beginning as $\delta E_{XC}/\delta \phi_{p}(2)$ has to be singular when $\epsilon_{HOMO} = \epsilon_{LUMO}$. For comparison, the OEP2sc result from *ab initio dft* is also shown, compared to the normally, poorly converged OEP2 based on the $H_{0}^{KS}$.

Other simplifications in the OEP solution are potentially possible. The most obvious is to make an Unsöld, constant energy denominator approximation(CEDA), replacing $\epsilon_{i} - \epsilon_{a} \approx \epsilon_{avg}$.(This should be contrasted with that of Kreiger-Li-Iafrate (KLI)[44] who made such an approximation in the Green’s function where the denominator consists of $\epsilon_{p} - \epsilon_{q}$ before simplifying the from to the occupied-virtual separation invoked here[16, 54, 57].) See Gritsenko, et al [56]. Such a constant energy denominator is a relatively painless approximation here, since $\epsilon_{avg}$ appears on both sides of eqn. (18), making it disappear from the equation for $V_{X}$. Once that is done, a resolution of the identity can be invoked to eliminate the virtual orbitals to give,

$$\sum_{i,a} \langle i|\hat{\rho}(a)|a\rangle|\hat{K} + \hat{V}_{X}|i\rangle = \sum_{i} \langle i|\hat{\rho}|\hat{K} + \hat{V}_{X}|i\rangle - \sum_{i,j} \langle i|\hat{\rho}|j\rangle \langle j|\hat{K} + \hat{V}_{X}|i\rangle$$
(5–33)
In this way, there is no dependence on the virtual orbitals as is deemed computationally or formally important in some DFT circles\cite{59} Of course, using the usual finite basis set computational tools of quantum chemistry, the distinction is less important. This formula has recently been applied\cite{58}.

Because the OEP equation is a point-wise identity having to be zero formally for all \( x \) in a finite basis set it corresponds to a many-to-few mapping in the general case. The dependence upon the delta function makes the OEP procedure sensitive to the auxiliary basis set used in the calculation. However, the SVD procedure handles the null space functions plus any potential linear dependency in the basis set in a fairly automatic way\cite{60}. If the \( X \) matrix is removed, this is not the case, and some algorithms can result in unphysical or trivial solutions under certain combinations of auxiliary and molecular bases. Choosing to invoke the average energy denominator and the resolution of the identity before the least-squares minimimization, will not give Eqn(24). However, once we eliminate the delta function that makes the approximation point-wise, we reduce the problem to the minimization of the variance

\[
\min Var = \min \sum_i \langle i | (\hat{K} + \hat{V}_X)^2 | i \rangle - \sum_{i,j} \langle i | \hat{K} + \hat{V}_X | j \rangle \langle j | \hat{K} + \hat{V}_X | i \rangle \quad (5-34)
\]

that can be used to define a \( V_X \), but one that is not point-wise, and, consequently, does not satisfy all the conditions above. This further simplification of the weighted least squares approach in Eqn (5–26) has also been considered recently \cite{58}. Ultimately, one primary criteria for the best exchange-only potential should be the satisfaction of the Janak theorem. As shown in Table 5-1, and pointed out previously\cite{16, 48} this is difficult to achieve in any normal basis set.
5.2 Time-Dependent Optimized Effective Potential

5.2.1 Theory and Implementation

Within the adiabatic approximation the TDOEP equations have the following matrix form (5–35)

\[
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
U \\
U^\dagger
\end{pmatrix}
= \omega
\begin{pmatrix}
U \\
U^\dagger
\end{pmatrix}
\] (5–35)

The matrices A and B have the following structure (5–36)

\[
A_{\alpha\sigma}^{ij\tau} = \delta_{ij}\delta_{\alpha\beta}(\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) + \langle a_{\sigma} b_{\tau}|i_{\sigma} j_{\tau} \rangle + \langle a_{\sigma} b_{\tau}|f_{\sigma\tau}|i_{\sigma} j_{\tau} \rangle
\]

\[
B_{\alpha\sigma}^{ij\tau} = \langle a_{\sigma} b_{\tau}|i_{\sigma} j_{\tau} \rangle + \langle a_{\sigma} b_{\tau}|f_{\sigma\tau}|i_{\sigma} j_{\tau} \rangle
\] (5–36)

where

\[
f_{\sigma\tau} = \delta_{\sigma\tau}\frac{\delta V^{OEP}_{\sigma}}{\delta \rho_{\tau}}\]

\[
\langle a_{\sigma} b_{\tau}|f_{\sigma\tau}|i_{\sigma} j_{\tau} \rangle = \delta_{\sigma\tau} \sum_{\kappa,\lambda,\mu,\nu} a_{\sigma} i_{\sigma} \kappa > (X^{-1})_{\kappa\lambda}(g_{\sigma})_{\lambda\mu}(X^{-1})_{\mu\nu} b_{\sigma} j_{\sigma} \nu > (5–38)
\]

with

\[
(g_{\sigma})_{\lambda\mu} = -2 \sum_{i,a,b} (K_{ia\sigma} + V^{OEP}_{ia\sigma}) \langle i_{\sigma} a_{\sigma} \lambda > i_{\sigma} b_{\sigma} \mu \rangle \frac{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{i\sigma} - \varepsilon_{b\sigma})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{a\sigma})}
\] + 2 \sum_{i,j,a} (K_{ij\sigma} + V^{OEP}_{ij\sigma}) \langle i_{\sigma} a_{\sigma} \lambda > a_{\sigma} j_{\sigma} \mu \rangle \frac{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{i\sigma} - \varepsilon_{b\sigma})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{a\sigma})}
\] - 2 \sum_{i,a,b} (K_{ia\sigma} + V^{OEP}_{ia\sigma}) \langle b_{\sigma} a_{\sigma} \lambda > i_{\sigma} b_{\sigma} \mu \rangle + \langle i_{\sigma} b_{\sigma} \lambda > b_{\sigma} a_{\sigma} \mu \rangle \frac{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{i\sigma} - \varepsilon_{b\sigma})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{a\sigma})}
\] + 2 \sum_{i,j,a} (K_{ij\sigma} + V^{OEP}_{ij\sigma}) \langle i_{\sigma} j_{\sigma} \lambda > a_{\sigma} j_{\sigma} \mu \rangle + \langle i_{\sigma} j_{\sigma} \mu > a_{\sigma} j_{\sigma} \lambda \rangle \frac{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{a\sigma})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{b\sigma})}
\] - 2 \sum_{i,j,a,b} \langle i_{\sigma} j_{\sigma} | b_{\sigma} a_{\sigma} \rangle + \langle i_{\sigma} a_{\sigma} | j_{\sigma} b_{\sigma} \rangle \langle i_{\sigma} a_{\sigma} \lambda > j_{\sigma} b_{\sigma} \mu \rangle \frac{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{b\sigma})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{b\sigma})}
\] (5–39)

Once the eigenvalue problem (5–35) is solved, we have the set of excitation energies, \( \omega \).
When we need to calculate polarizabilities at frequency $\omega$, the following system of linear equations (5–40) should be solved

$$\begin{pmatrix} A - \omega 1 & B \\ B & A + \omega 1 \end{pmatrix} \begin{pmatrix} d^{\omega -} \\ d^{\omega +} \end{pmatrix} = - \begin{pmatrix} h \\ h \end{pmatrix}$$

(5–40)

where

$$h_{pq\sigma} = \int dr \varphi_{p\sigma}(r) \vec{r} \varphi_{q\sigma}(r)$$

(5–41)

Once these equations are solved for $d$, the dynamic polarizability is readily evaluated from

$$\alpha(-\omega; +\omega) = - \sum_{i,a} \sum_{\sigma} (h_{ia\sigma}d_{ia\sigma}^{\omega -} + h_{ia\sigma}d_{ia\sigma}^{\omega +})$$

(5–42)

For the calculation of the $C_6$ van der Waals coefficients, the system of equations (5–40) should be solved for the imaginary frequencies $i\omega$ from which the coefficients can be calculated by

$$C_6^{\alpha\alpha} = \frac{3}{\pi} \int_0^\infty d\omega \alpha(i\omega) \alpha(i\omega)$$

(5–43)

where $\alpha(i\omega) = \frac{1}{3}(\alpha_{xx}(i\omega) + \alpha_{yy}(i\omega) + \alpha_{zz}(i\omega))$. Integration of equation (5–43) was carried out by Gauss-Chebyshev quadrature.

To ensure the correct $-\frac{1}{r}$ asymptotic behavior of the exchange potential, the Colle-Nesbet algorithm[30] was used. As a seed potential, we used the one proposed by Slater[38]

$$V_{\sigma}^{Slater}(r) = \sum_{i,j} \frac{\varphi_{i\sigma}(r) \varphi_{j\sigma}(r)}{\rho_\sigma} \int dr_1 \frac{\varphi_{i\sigma}(r_1) \varphi_{j\sigma}(r_1)}{|r - r_1|}$$

(5–44)

For the spin-polarized case two different Slater potentials are used for the corresponding spin component of the local exchange.

5.2.2 Numerical Results

Excitation energies and polarizabilities are calculated for several open-shell systems. Equilibrium geometries are taken from ref[36]. For all calculations the uncontracted
ROOS-ADZP basis set[27] has been used. Results for excitation energies are presented in Table 5-3.

Table 5-3. Excitation energies (V - valence state, R - Rydberg)

<table>
<thead>
<tr>
<th></th>
<th>TDHF</th>
<th>$\varepsilon_{i}^{OEP} - \varepsilon_{a}^{OEP}$</th>
<th>TDOEP</th>
<th>SVWN</th>
<th>CCSD</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2\Pi$(V)</td>
<td>4.18</td>
<td>8.16</td>
<td>4.91</td>
<td>1.96</td>
<td>1.52</td>
<td>1.32</td>
</tr>
<tr>
<td>$^2\Sigma^+$(V)</td>
<td>5.47</td>
<td>10.58</td>
<td>5.48</td>
<td>3.19</td>
<td>3.62</td>
<td>3.22</td>
</tr>
<tr>
<td>$CO^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2\Pi$(V)</td>
<td>7.55</td>
<td>9.98</td>
<td>8.23</td>
<td>3.03</td>
<td>3.43</td>
<td>3.26</td>
</tr>
<tr>
<td>$^2\Sigma^+$(V)</td>
<td>11.14</td>
<td>9.37</td>
<td>10.82</td>
<td>4.99</td>
<td>6.14</td>
<td>5.82</td>
</tr>
<tr>
<td>$CH_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2A_1'$ (R)</td>
<td>6.52</td>
<td>6.53</td>
<td>6.42</td>
<td>5.00</td>
<td>5.88</td>
<td>5.72</td>
</tr>
<tr>
<td>$^2A_2^+$ (R)</td>
<td>7.93</td>
<td>7.97</td>
<td>7.93</td>
<td>5.93</td>
<td>7.18</td>
<td>7.44</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4P$ (V)</td>
<td>9.84</td>
<td>11.11</td>
<td>9.88</td>
<td>10.98</td>
<td>10.84</td>
<td>10.35</td>
</tr>
<tr>
<td>$^4P$ (R)</td>
<td>13.59</td>
<td>13.16</td>
<td>13.18</td>
<td>11.76</td>
<td></td>
<td>13.62</td>
</tr>
</tbody>
</table>

As follows from the first two columns of Table 5-3, TDHF and TDOEPx produce results of approximately the same accuracy, as would be expected by the fact that the local exchange in TDOEP is meant to be a kind of least-squares fit to the HF non-local exchange potential. This certainly makes the occupied orbitals quite similar, but the spectrum of unoccupied orbital eigenvalues is very different, as shown in Table 5-4, since TDOEPx will generate a Rydberg type series instead of anything like the HF virtuals. As is well known, the latter are determined in a potential of n-electrons, making them appropriate for electron attached states, while the occupied ones feel a potential of n-1 electrons. To the contrary, the orbitals obtained in OEPx have the same potential for an electron in the occupied and unoccupied orbitals, which is why the latter more nearly simulate Rydberg states, as some of the unoccupied orbitals will have negative orbital energies. Of course, in a finite basis as long as the space separately spanned by the occupied and the unoccupied orbitals is the same, there would be no difference in the results, though the diagonal values (but not the trace) would change. The significant

---

1 This Rydberg state was not obtained in the EOM - CCSD Davidson diagonalization
Table 5-4. Orbital energies (in e. v.) of Ne atom

<table>
<thead>
<tr>
<th></th>
<th>OEPx</th>
<th>HF</th>
<th>EOM-CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>-839.67</td>
<td>-891.78</td>
<td>-871.11</td>
</tr>
<tr>
<td>2s</td>
<td>-47.36</td>
<td>-52.52</td>
<td>-48.11</td>
</tr>
<tr>
<td>2p</td>
<td>-23.74</td>
<td>-23.14</td>
<td>-21.28</td>
</tr>
<tr>
<td>3s(3p)</td>
<td>-5.21</td>
<td>3.66</td>
<td>3.70</td>
</tr>
<tr>
<td>3p(3s)</td>
<td>-3.11</td>
<td>3.94</td>
<td>3.62</td>
</tr>
<tr>
<td>4p</td>
<td>5.66</td>
<td>16.08</td>
<td>15.66</td>
</tr>
</tbody>
</table>

discrepancies with the experimental data can be explained by the fact that electron correlation effects are not introduced by either TDHF or TDOEP. To get some measure of the correlation effect, coupled cluster (CC) results from EOM-CCSD are reported[61], and the Slater-Vosko-Wilk-Nusiar (SWVN) functional is also used. The latter produces good results for valence states, but the energies of the Rydberg states are underestimated. This underestimation is a consequence of the incorrect asymptotic behavior of the SWVN potential, for which Janak’s theorem is not satisfied (see Table 5-5) and is a well-known characteristic that standard exchange-correlation potentials do not offer a Koopmans-type approximation for the orbital energies. However for OEP exchange-only and with correlation, it has been proven that the orbital energies offer a meaningful Koopmans approximation to principal IP’s for the valence and mid-valence states [16], so Rydberg states should potentially be better described. Of course, definitive comparison would require OEP with correlation as presented elsewhere[62], and this is seen in the OEP2-sc orbital energies[16, 48], but a full TDOEP treatment of excited states[62] requires the correlation kernel. This does not appear to be a viable route yet.

Table 5-5. Ionization energies (in e. v.)

<table>
<thead>
<tr>
<th></th>
<th>HOMO</th>
<th></th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF</td>
<td>OEP</td>
<td>SVWN</td>
</tr>
<tr>
<td>$CH_3$</td>
<td>10.46</td>
<td>11.19</td>
<td>5.38</td>
</tr>
<tr>
<td>N</td>
<td>15.53</td>
<td>16.14</td>
<td>8.41</td>
</tr>
</tbody>
</table>

Results for the polarizabilities and $C_6$ coefficients are presented in Tables 5-6 and 5-7. In all cases, the static polarizabilities obtained with TDOEP are very close to the
TDHF ones. For both excitation energies and polarizabilities this closeness arises from the fact that the OEP potential derived from the HF energy functional and its time-dependent response properties are similar. Systematic overestimation of polarizabilities is also caused by the lack of the $-\frac{1}{r}$ asymptotic dependence. In most cases this causes an even larger error than that coming from the absence of correlation effects in TDHF and TDOEP. The anisotropy of the polarizability, though, is usually reproduced much better by SVWN. This fact must be due to cancellation of errors, coming from the incorrect asymptotic and incomplete cancellation of self-interaction error, plus a proper accounting of correlation effects.

5.2.3 Charge-Transfer Excited States

Within the framework of the standard TDDFT description of excited states the transfer of charge between two separated fragments has severe difficulties. Detailed analysis of this problem has been presented by Tozer[63] and Dreuw et al[51]. According to the latter analysis [51] even if the exact exchange-correlation functional were known, it would still be impossible to get a proper description of charge-transfer excitations within TDDFT. Consider the example of He ... Be. The charge-transfer $^1\Pi$ state calculated with TDHF and TDOEP, taken with the Tamm-Dancoff (mono-excited CI) approximation for simplicity. For both atoms the uncontracted ROOS-ADZP basis set was used. Potential curves of the $^1\Pi$ charge-transfer excited state are presented on Fig 5-2. The potential curve, calculated with the configuration interaction singles method exhibits the correct $-\frac{1}{R}$ long-range asymptotic behavior, while the TDOEP results have a qualitatively wrong asymptotic behavior. This phenomena is caused by the fact that for charge-transfer excitations all integrals in Eqn. (5–36) are equal to zero and the excitation frequency is equal to the difference of the LUMO orbital energy of the Be atom and the HOMO energy of the He atom.

What was not addressed numerically in Dreuw et al[51] was the effect of having a proper self-interaction and asymptotic behavior in DFT, which can only be achieved
Figure 5-2. A $^1\Pi$ charge-transfered excited state of He ... Be

with OEP methods. We report those in Fig 5-3. Obviously, the orbital energy difference

Figure 5-3. LUMO-HOMO orbital energy difference

behaves very differently for OEP and HF since in both cases the HOMO orbital energy corresponds to an ionization potential approximation, but the LUMO energy corresponds to a Rydberg state approximation for the OEP method and to an approximate electron
affinity in the case of HF. If one considers the LUMO-HOMO energy difference as a zero-order approximation to the excitation energy and the rest of matrix elements in Eqn. (5–36) as corrections, it is apparent that TDDFT has a qualitatively wrong behavior in each order when dealing with charge-transfer excitations.

If one argues that the occupied orbitals in the HF and OEP calculations are nearly the same, and they span the occupied space, then the unoccupied space would be the same, too. However, even if the spaces were the same, the difference between the non-local \( \hat{K} \) and local \( \hat{V}_x \) is sufficient to keep the latter local exchange from ever being able to describe an electron attached state. Thus, it is not possible to overcome the local operator’s failure even in the full space for the calculations.

5.3 Conclusions

In this article some possible formulations of OEP are stressed. It was argued and shown numerically that the OEP formulations which adhere to the requirement of pointwise closeness of local and non-local exchange potentials are far more stable to variations in the molecular and auxiliary basis sets, and do not suffer from arbitrary limitations on the choice of basis. However, the OEP problem remains ill-conditioned, as also stated previously[16, 52], and does require the use of a generalized (SVD) inverse or the equivalent. It was also shown that under the right conditions the exact HF result can be obtained by an OEP-like procedure as a trivial solution of a weighted least squares procedure. Any point-wise condition has to be a many to few mapping in a finite basis set.

The elimination of denominators from working expressions for OEPx [20, 44, 56] can be done as shown, to obtain the computational advantage of using only the occupied orbitals in the OEP procedure. The direct optimization algorithm as implemented, however, has led to work [45, 49] that has suggested incorrect conclusions.

The TDOEP method was implemented for spin-polarized open-shell systems. Results for several open-shell systems show very similar time-dependent behavior for the time-dependent response of the OEP and the HF potentials. The correct long-range
asymptotic behavior, achieve by the Colle-Nesbet algorithm, makes it possible to avoid an underestimation of Rydberg state energies and overestimation of the polarizabilities. This overestimation for polymers, particularly for hyperpolarizabilities, has attracted a great deal of attention\[64–66\]

The problem of charge-transfer excited states in TDDFT relates to the inability of the zeroth-order orbital energy approximations, as the HF virtual orbitals and TDOEP excited orbitals show qualitatively different behavior. If the HF and OEP operators were the same, a proper treatment using the whole space should be able to overcome this limitation, even if the usual zeroth-order approximation offered by TDDFT would be a poor one. However, this difference arises from the form of the operator, local versus non-local, and, as such, remains a fundamental problem for the DFT method itself, as has been observed \[51\]

In conclusion, for all the properties considered in the paper, except for charge-transfer excited states, there seems to be no significant difference between the results of TDHF and exchange-only TDOEP, as one might expect. Hence, the focus should remain on the correlation potential as it is in ab initio dft\[16, 17, 48, 62\].
Table 5-6. Static polarizabilities (in a. u.)

<table>
<thead>
<tr>
<th></th>
<th>TDHF</th>
<th>TDOEP</th>
<th>SVWN</th>
<th>CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>11.98</td>
<td>11.91</td>
<td>15.63</td>
<td>12.50</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>11.98</td>
<td>11.91</td>
<td>15.63</td>
<td>12.50</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>18.55</td>
<td>18.41</td>
<td>25.00</td>
<td>23.42</td>
</tr>
<tr>
<td>$\bar{\alpha}$</td>
<td>14.17</td>
<td>14.08</td>
<td>18.75</td>
<td>16.16</td>
</tr>
<tr>
<td>$\Delta \alpha$</td>
<td>6.57</td>
<td>6.50</td>
<td>9.38</td>
<td>10.94</td>
</tr>
<tr>
<td>$CO^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>6.66</td>
<td>6.66</td>
<td>9.38</td>
<td>9.38</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>6.66</td>
<td>6.66</td>
<td>9.38</td>
<td>9.38</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>12.22</td>
<td>12.15</td>
<td>14.06</td>
<td>12.50</td>
</tr>
<tr>
<td>$\bar{\alpha}$</td>
<td>8.52</td>
<td>8.49</td>
<td>10.94</td>
<td>10.42</td>
</tr>
<tr>
<td>$\Delta \alpha$</td>
<td>5.54</td>
<td>5.50</td>
<td>4.69</td>
<td>3.13</td>
</tr>
<tr>
<td>$CH_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>15.06</td>
<td>15.00</td>
<td>18.75</td>
<td>15.63</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>14.04</td>
<td>13.98</td>
<td>18.75</td>
<td>15.63</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>15.06</td>
<td>15.00</td>
<td>18.75</td>
<td>15.63</td>
</tr>
<tr>
<td>$\bar{\alpha}$</td>
<td>14.72</td>
<td>14.66</td>
<td>18.75</td>
<td>15.63</td>
</tr>
<tr>
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<td>1.02</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>6.24</td>
<td>6.23</td>
<td>6.25</td>
<td>5.94</td>
</tr>
</tbody>
</table>

Table 5-7. Isotropic $C_6$ coefficients (in a. u.)

<table>
<thead>
<tr>
<th></th>
<th>TDHF</th>
<th>TDOEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>93.97</td>
<td>92.06</td>
</tr>
<tr>
<td>$CH_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>94.27</td>
<td>93.40</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>19.28</td>
<td>19.21</td>
</tr>
</tbody>
</table>

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CHAPTER 6
EXACT-EXCHANGE TIME-DEPENDENT DENSITY FUNCTIONAL THEORY FOR
HYPERPOLARIZABILITIES

The time-dependent OEP exchange-only method (OEPx) has been previously
derived by Görling\cite{20} and implemented for molecules by Hirata \textit{et. al} \cite{21, 50}. Numerical
results in the latter papers show a reasonable description of both valence and Rydberg
excited states. Reasonable static and dynamic polarizabilities are also obtained. Good
results of TDOEPx for excited states and properties are obtained partly due to the correct
asymptotic behavior of the exchange potential, but also due to the elimination of the
self-interaction error. In particular, OEP-TDDFTx tends to be superior to standard
approaches like TDDFT based upon the local density approximation (LDA) or Becke-Lee-
Yang-Parr (BLYP) functionals. Similarly, exchange-only OEP with exact local exchange
(EXX)\cite{22, 23} has been shown to greatly improve band-gaps in polymers \cite{23}

Another advantage of OEP based methods is that since virtual orbitals in the
exchange-only DFT as well as the occupied orbitals are generated by a local potential,
which corresponds to the N-1 particle system due to the satisfaction of the self-interaction
cancellation, the differences between orbital energies of virtual and occupied orbitals
offer a good zeroth-order approximation to the excitation energies\cite{16, 17}. This is not
possible in the case of Hartree-Fock theory, without adding a $V^{N-1}$ potential\cite{67, 68},
since occupied orbitals are generated by an N-1 particle potential and the energies of
unoccupied orbitals come from N-electron potential, and thereby, approximate electron
affinities.

In Kohn-Sham DFT

\[ h_{KS} = \hat{T} + \hat{V}_{\text{ext}} + \hat{J} + \hat{V}_{xc} \]
where
\[
\hat{V}_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)}
\]
\[
\hat{J}\varphi(r) = \int dr' \frac{\varphi(r)\rho(r')}{|r-r'|}
\]
To address second-order properties requires additional effects of the density change given as the second and higher terms of Taylor’s expansion of \(E_{xc}\). The kernel
\[
f_{x}(r_{1}, r_{2}) = \frac{\delta V_{xc}(r_{1})}{\delta \rho(r_{2})}
\]
is used in [21, 50]. However, once our objective is third-order molecular property, the essential new element in TDDFT is the second exchange-correlation kernel, which in an adiabatic approximation is defined as the second functional derivative of the exchange-correlation potential with respect to the density
\[
g(r_{1}, r_{2}, r_{3}) = \frac{\delta V_{xc}(r_{1})}{\delta \rho(r_{2})\delta \rho(r_{3})}
\]
Hence, in this paper we will derive the second kernel for the exact-exchange DFT, based on the OEPx approach. This is a complicated quantity. The traditional way of deriving kernels and potentials is to tediously derive all terms with the use of the chain-rule for functional differentiation. Yet, even the exchange-only kernel, \(f\), has a complicated structure in OEP, and its further extension to a second kernel is very difficult. To avoid the use of traditional methods, an effective diagrammatic formalism for taking functional derivatives was recently developed[37, 62]. In this paper we use that formalism and apply it to the exchange second kernel for OEPx based time-dependent DFT. After discussing some properties of the second kernel, we report numerical results to obtain hyperpolarizabilities, compared to those from Hartree-Fock and coupled cluster singles and doubles (CCSD).

There is a long history of the treatment of hyperpolarizabilities and associated nonlinear optical (NLO) properties. See [69] for a review. In particular, issues of the incorrect
behavior of TDDFT hyperpolarizabilities for NLO design for polymers\cite{64, 65} points to
the necessity of an improved theory. A rigorous (\textit{ab initio}) DFT analogue starts with
exchange-only, TDDEPx.

\section{Theory}

\subsection{Time-Dependent Density Functional Theory Response Properties}

When an external time-dependent electric field is applied, the perturbation can be
written in the form (6–2)

\[ V(t) = -\sum_i \vec{r}_i \cdot \vec{E}(t) \] (6–2)

For the case of periodic perturbations, the virtual-occupied block of the linear response of
the density can be found from the following system of linear equations

\[ (\mathbf{A} + \mathbf{B}) \mathbf{U} = -\mathbf{h} \] (6–3)

The matrices \( \mathbf{A}, \mathbf{B} \) have the structure, given by Eqn (5–36) and \( \mathbf{h} \) is

\[ h_{a i \sigma} = < a_{\sigma} | \vec{r} | i_{\sigma} > \] (6–4)

The calculation of the components of the first, static hyperpolarizability tensor
requires \cite{70}

\[ \beta_{\lambda \mu \nu} = 2 \sum_{i,p,q,\sigma} (U_{i \sigma}^\lambda \tilde{F}_{pq}^\mu U_{q \sigma}^{\nu'} + U_{i \sigma}^\lambda \tilde{F}_{pq}^{\nu'} U_{q \sigma}^\mu + U_{i \sigma}^\nu \tilde{F}_{pq}^\mu U_{q \sigma}^{\lambda} +
\]

\[ U_{i \sigma}^{\nu'} \tilde{F}_{pq}^\lambda U_{q \sigma}^\mu + U_{i \sigma}^\nu \tilde{F}_{pq}^\lambda U_{q \sigma}^\mu + U_{i \sigma}^{\lambda} \tilde{F}_{pq}^\mu U_{q \sigma}^{\nu'} +
\]

\[ -2 \sum_{i,j,p,\sigma} (U_{pi \sigma}^{\lambda} \tilde{\epsilon}_{ij}^{\nu'} U_{jp \sigma}^{\mu} + U_{pi \sigma}^{\lambda} \tilde{\epsilon}_{ij}^{\nu'} U_{jp \sigma}^{\mu} + U_{pi \sigma}^{\nu} \tilde{\epsilon}_{ij}^{\lambda} U_{jp \sigma}^{\mu} +
\]

\[ U_{pi \sigma}^{\nu} \tilde{\epsilon}_{ij}^{\lambda} U_{jp \sigma}^{\mu} + U_{pi \sigma}^{\lambda} \tilde{\epsilon}_{ij}^{\nu'} U_{jp \sigma}^{\mu} + U_{pi \sigma}^{\nu} \tilde{\epsilon}_{ij}^{\lambda} U_{jp \sigma}^{\mu} +
\]

\[ 8 \sum_{\sigma} \sum_{a,b,c,i,j,k} < \varphi_{a \sigma} \varphi_{b \sigma} \varphi_{c \sigma} | g_{\sigma} | \varphi_{i \sigma} \varphi_{j \sigma} \varphi_{k \sigma} > U_{a i \sigma}^{\lambda} U_{b j \sigma}^{\mu} U_{c k \sigma}^{\nu'} \] (6–5)
The matrix elements $F_{pq\sigma}^\lambda$ and $\bar{\epsilon}_{ij\sigma}^\lambda$ can be calculated from the relations (6–6)

$$F_{pq\sigma}^\lambda = h_{pq\sigma}^\lambda + \sum_{a,i} (A_{pq\sigma}^{ai\sigma} + B_{pq\sigma}^{ai\sigma}) U_{ai\sigma}^\lambda$$

(6–6)

$$\bar{\epsilon}_{ij\sigma}^\lambda = \bar{F}_{ij\sigma}^\lambda$$

(6–7)

### 6.1.2 Diagrammatic Derivation of the Second Exact-Exchange Kernel

For the derivation of the second kernel it is convenient to use the form (6–8)

$$g(r_1, r_2, r_3) = \delta f_{xc}(r_1, r_2)$$

(6–8)

Which can be rewritten as

$$\frac{\delta f_{xc}(r_1, r_2)}{\delta \rho(r_3)} = \int dr_4 dr_5 \frac{\delta X^{-1}(r_1, r_4)}{\delta \rho(r_3)} Q(r_4, r_5) X^{-1}(r_5, r_2) +$$

$$\int dr_4 dr_5 X^{-1}(r_1, r_4) \frac{\delta Q(r_4, r_5)}{\delta \rho(r_3)} X^{-1}(r_5, r_2) +$$

$$\int dr_4 dr_5 X^{-1}(r_1, r_4) Q(r_4, r_5) \frac{\delta X^{-1}(r_5, r_2)}{\delta \rho(r_3)}$$

(6–9)

Taking into account the fact that

$$\frac{\delta X^{-1}(r_1, r_2)}{\delta \rho(r_3)} = -\int dr_4 dr_5 X^{-1}(r_1, r_5) \frac{\delta X(r_5, r_4)}{\delta V_s(r_3)} X^{-1}(r_2, r_4)$$

(6–10)

and doing some simple transformations, it is possible to write

$$g(r_1, r_2, r_3) = -\int dr_6 dr_7 dr_8 f(r_2, r_8) X^{-1}(r_3, r_6) \frac{\delta X(r_7, r_8)}{\delta V_s(r_6)} X^{-1}(r_1, r_7) +$$

$$\int dr_4 dr_5 dr_6 X^{-1}(r_1, r_4) X^{-1}(r_3, r_6) \frac{\delta Q(r_4, r_5)}{\delta V_s(r_6)} X^{-1}(r_2, r_5) -$$

$$\int dr_6 dr_7 dr_8 f(r_1, r_7) X^{-1}(r_3, r_6) \frac{\delta X(r_7, r_8)}{\delta V_s(r_6)} X^{-1}(r_2, r_8)$$

(6–11)

where

$$V_s(r) = v_{ext}(r) + \int dr' \frac{\rho(r')}{|r - r'|} + V_{xc}(r)$$

(6–12)
The first element of Eqn (6–11) can be written as

\[- \int dr_6dr_7dr_8f(r_2,r_8)X^{-1}(r_3,r_6)\frac{\delta X(r_7,r_8)}{\delta V_s(r_6)}X^{-1}(r_1,r_7) = \]

\[- \int dr_6dr_7X^{-1}(r_3,r_6)P_1(r_2,r_6,r_7)X^{-1}(r_1,r_7) \]  

(6–13)

and \(P_1(r_2,r_6,r_7)\) can be presented as a sum of diagrams (F1) - (F6) of (6–14)

\[
\begin{align*}
(F1) & \quad \delta(r_6) \\
(F2) & \quad \delta(r_7) \\
(F3) & \quad \delta(r_7) \\
(F4) & \quad \delta(r_7) \\
(F5) & \quad \delta(r_7) \\
(F6) & \quad \delta(r_7)
\end{align*}
\]

(6–14)

In the same way the third term of eq (16) can be rewritten as

\[- \int dr_6dr_7dr_8f(r_1,r_7)X^{-1}(r_3,r_6)\frac{\delta X(r_7,r_8)}{\delta V_s(r_6)}X^{-1}(r_2,r_8) = \]

\[- \int dr_6dr_7X^{-1}(r_3,r_6)P_2(r_1,r_6,r_7)X^{-1}(r_2,r_7) \]  

(6–15)

where \(P_2(r_1,r_6,r_7)\) gives the sum of diagrams (F7) - (F12) of (6–16)

\[
\begin{align*}
(F7) & \quad \delta(r_6) \\
(F8) & \quad \delta(r_7) \\
(F9) & \quad \delta(r_7) \\
(F10) & \quad \delta(r_7) \\
(F11) & \quad \delta(r_7) \\
(F12) & \quad \delta(r_7)
\end{align*}
\]

(6–16)

The diagrammatic expression for \(Q(r_6,r_7)\) contains terms (V1) - (V6) and (FX1) - (FX8) of (6–17) and (6–18)[62]
Functional derivatives from the set (V1)-(V6) can be presented by two types of diagrams.

The first type contains the exchange kernel, diagrams (F13)-(F18) of (6–19)

\[
\begin{align*}
& \delta(r_4) \quad \delta(r_5) \quad \delta(r_6) \\
& (F13) \quad (F14) \quad (F15) \quad (F16) \quad (F17) \quad (F18)
\end{align*}
\]

The second type contains the exchange potential, giving diagrams (VX1)-(VX8) of (6–20)

\[
\begin{align*}
& \delta(r_4) \quad \delta(r_5) \quad \delta(r_6) \\
& (VX1) \quad (VX2) \quad (VX3) \quad (VX4) \quad (VX5) \quad (VX6) \quad (VX7) \quad (VX8)
\end{align*}
\]

The notation \( r_4 \backslash r_5 \backslash r_6 \) means that for each particular diagram all six permutations of \( r_4, r_5 \) and \( r_6 \) should be taken. The functional derivatives from diagrams (FX1)-(FX8) lead to the set (SX1)-(SX14) of (6–21) and (6–22).

\[
\begin{align*}
& \delta(r_4) \quad \delta(r_5) \quad \delta(r_6) \\
& (SX1) \quad (SX2) \quad (SX3) \quad (SX4) \quad (SX5) \quad (SX6) \quad (SX7) \quad (SX8) \quad (SX9)
\end{align*}
\]
Interpretation of all diagrams which contributes into the second kernel and details of the implementation are given in Appendix B.

### 6.1.3 Properties of the Second Exact-Exchange Kernel

All the diagrams contributing to the second exact-exchange kernel have only one contour and because of this fact only $\alpha\alpha\alpha$ and $\beta\beta\beta$ spin components are present, as in Goldstone diagrams where $S_z$ has to be conserved at each vertex. The algebraic expressions for all the diagrams have to be symmetric with respect to permutations of $r_1, r_2,$ and $r_3$ variables. In the case of the two-electron spin-unpolarized systems the OEP exchange potential becomes equivalent to the Slater potential\cite{38}

$$V_{\sigma}^{\text{Slater}}(r) = - \sum_{i,j} \frac{\varphi_{ia}(r)\varphi_{ja}(r)}{\rho_\sigma} \int d\mathbf{r}_1 \frac{\varphi_{ia}(\mathbf{r}_1)\varphi_{ja}(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} \quad (6–23)$$

Taking into account the HOMO condition and considering the expression for the exchange kernel, it is possible to write for the special case of two electrons

$$f_{\sigma}^{\text{OEP}}(r_1, r_2) = - \frac{1}{|r_1 - r_2|} \quad (6–24)$$

Diagrams (VX1)-(VX5) and (VX8) of (6–20) will cancel diagrams (SX7), (SX8) and (SX11)-(SX14) of (6–21) and (6–22) because of the HOMO condition and the behavior of the Hartree-Fock exchange for the case of two electrons. Diagrams (VX6) and (VX7) will cancel diagrams (SX1) and (SX2) because of Eqn (6–23). Diagrams (SX5), (SX6), (SX9) and (SX10) will cancel diagrams (F1)-(F4), (F7)-(F10) and (F13)-(F16) because of Eqn (6–24). Finally the sum of the diagrams (SX3) and (SX4) cancel the sum of (F5), (F6), (F11), (F12), (F17) and (F18). Thus for the special case of two electrons

$$g_{\sigma}^{\text{OEP}}(r_1, r_2, r_3) \equiv 0 \quad (6–25)$$
The condition (6–25) might be used as a hint for developing new density functionals, as none of the existing functionals exhibit such behavior.

### 6.2 Numerical Results

As a numerical test the static hyperpolarizabilities of LiH, $H_2O$, CO and CN are calculated. In all cases uncontracted ROOS-ADZP basis sets\[^{27}\] are used and equilibrium geometries are taken from ref\[^{36}\]. The results calculated with different methods are presented in Table 6-1. In the first four columns are static hyperpolarizabilities obtained with Hartree-Fock non-local exchange and with the two local exchange operators: OEP-HF, which means equation (6–5) without the second kernel term, and OEPx, which means all terms in equation (6–5). The hyperpolarizability values calculated with the OEPx method are in good agreement with the corresponding Hartree-Fock values, and generally no better. This good agreement can be explained by the fact that OEPx method is free from the self-interaction error, has the correct long-range asymptotic behavior, and the correct HOMO values. As hyperpolarizabilities are response properties of third order their calculation within the DFT method requires very precise exchange-correlation potentials. Only potentials which simultaneously satisfy all theorems and conditions pertaining to the DFT exchange potentials can be expected to reproduce even the Hartree-Fock

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>OEP-HF</th>
<th>OEPx</th>
<th>LDA</th>
<th>CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{zzz}$</td>
<td>312.130</td>
<td>314.910</td>
<td>312.126</td>
<td>621.093</td>
<td>691.406</td>
</tr>
<tr>
<td>$\beta_{xxx}$</td>
<td>201.150</td>
<td>207.868</td>
<td>201.641</td>
<td>404.297</td>
<td>204.171</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{zzz}$</td>
<td>-31.016</td>
<td>-24.864</td>
<td>-29.455</td>
<td>-66.406</td>
<td>27.343</td>
</tr>
<tr>
<td>$\beta_{xxx}$</td>
<td>-3.073</td>
<td>-4.660</td>
<td>-3.118</td>
<td>-13.203</td>
<td>5.859</td>
</tr>
<tr>
<td>CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{zzz}$</td>
<td>-1.299</td>
<td>0.211</td>
<td>-3.906</td>
<td>-1.953</td>
<td>164.02</td>
</tr>
<tr>
<td>$\beta_{xxx}$</td>
<td>-17.651</td>
<td>-15.646</td>
<td>-18.121</td>
<td>-62.500</td>
<td>68.359</td>
</tr>
<tr>
<td>$H_2O$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{zzz}$</td>
<td>-6.713</td>
<td>-6.239</td>
<td>-7.812</td>
<td>-13.672</td>
<td>-5.859</td>
</tr>
<tr>
<td>$\beta_{xxx}$</td>
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<td>-0.604</td>
<td>-1.215</td>
<td>-6.138</td>
<td>-3.870</td>
</tr>
<tr>
<td>$\beta_{yyz}$</td>
<td>-10.866</td>
<td>-10.32</td>
<td>-11.847</td>
<td>-23.437</td>
<td>-7.645</td>
</tr>
</tbody>
</table>
hyperpolarizabilities. The large errors of the LDA method are caused by the wrong long-range asymptotic behavior and the incomplete cancellation of the self-interaction terms, though LDA does reflect some estimate of correlation. In ref[66] it was pointed out that none of the existing hybrid and asymptotically corrected functionals are capable of reproducing Hartree-Fock hyperpolarizabilities. The semi-empirical method, developed there[66] is the only known way to get reasonable hyperpolarizabilities with conventional functionals. However, the OEPx potentials and kernels are the only rigorous, purely ab initio way to obtain high-order properties, within a solely DFT framework of local potentials and kernels.

For the calculation of hyperpolarizabilities with the Hartree-Fock method[71] the last term in eq (6–5) should be dropped. Its importance for the DFT scheme can be estimated from the second column of Table 6-1, where OEP hyperpolarizabilities were calculated without the last term of equation (6–5). For the example of the LiH molecule the relative contribution of the last term is small. However, going from closed shell to an open-shell, like for the CN molecule, the relative contribution of the third kernel becomes much greater and, sometimes, can even change the sign of hyperpolarizabilities.

The differences between the OEPx and the coupled cluster singles and doubles (CCSD) method are because in the exchange-only OEP method electron correlation has not been taken into account. For the calculation of high-order properties, which can be compared with experimental data, accounting for the electron correlation is critical [69, 72, 73], and generally CCSD is fairly good, though adding triples offer some improvement. Nevertheless, the present results show what kind of properties exchange potentials and kernels must have to be able to describe higher-order properties within the framework of DFT, and as mentioned previously, none of the current set of functionals for standard DFT shows this behavior.
6.3 Conclusions

We have presented the analytical expressions and implemented them for the calculations of static hyperpolarizabilities applicable to general molecular systems with the exact exchange functional of Kohn-Sham DFT through the TDOEPx formalism, the first step in the application of *ab initio dft*\[16\] It has been shown that the rigorous exchange treatment in TDOEP and TDHF provide hyperpolarizabilities that closely agree with each other, as one would expect, although this will not happen for charge-transfer excited states\[51, 74\]. This clear agreement with TDHF is in contrast to conventional exchange functionals that severely overestimate hyperpolarizabilities. OEP potentials and kernels are not only capable of describing excitation energies, but also higher-order properties. Since none of the standard DFT functionals shows the correct analytic properties of the second kernel, the OEP formulas and results can be used for the testing and calibration of new density functionals.
APPENDIX A
INTERPRETATION OF DIAGRAMS OF THE SECOND-ORDER MANY-BODY PERTURBATION THEORY OPTIMIZED EFFECTIVE POTENTIAL CORRELATION KERNEL

To build $h(r_3, r_6)$ we have to provide the summation of the diagrams contributing into the correlation kernel. The time - dependent OEP-MBPT(2) equations are implemented, using a gaussian basis set. Kernels and potentials are decomposed using the auxiliary basis set

$$V_{xc}(r) = \sum_{\lambda} C_{\lambda} \xi_{\lambda}(r)$$

$$X(r_1, r_2) = \sum_{\nu,\kappa} X_{\nu\kappa} \xi_{\nu}(r_1) \xi_{\kappa}(r_2)$$

$$f(r_1, r_2) = \sum_{\nu,\lambda,\mu} X_{\nu\lambda}^{-1} h_{\lambda\mu} X_{\mu\nu}^{-1} \xi_{\nu}(r_1) \xi_{\lambda}(r_2)$$

(A-1)

where

$$X_{\nu\kappa} = 2 \sum_{i,a} \left( \frac{\langle ia\nu \rangle \langle ia\kappa \rangle}{\varepsilon_i - \varepsilon_a} \right)$$

$$< pq\gamma > = \int dr \varphi_p(r) \varphi_q(r) \xi_{\gamma}(r)$$

(A-2)

$$(VC1 - 1) + (VC2 - 2) = -2 \sum_{a,b,c,i,j,k} \frac{< ab|ij \rangle < c j|ak > ( < ic\lambda > < k b\mu > + < kb\lambda > < i c\mu > )}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_b)}$$

(A-3)

$$(VC1 - 2) = 2 \sum_{a,b,c,d,i,j} \frac{< ab|ij \rangle < c d|ab > < ic\lambda > < dj\mu >}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_j - \varepsilon_d)}$$

(A-4)

$$(VC1 - 3) + (VC3 - 1) = -2 \sum_{a,b,c,i,j,k} \frac{< ab|ik \rangle < c j|ab > ( < ic\lambda > < kj\mu > + < k j\lambda > < i c\mu > )}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)}$$

(A-5)
\[(VC1 - 4) + (VC4 - 1) = 2 \sum_{a,b,c,d,i,j} \frac{< ad | ij > < cj | ab > (< ic | λ > < db | µ > + < ic | µ > < db | λ >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_d)(\varepsilon_i - \varepsilon_c)} \quad (A-6)\]

\[(VC1 - 5) = 2 \sum_{a,b,c,d,i,j} \frac{< ab | id > < cj | ab > < ic | λ > < dj | µ >}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_j - \varepsilon_d)} \quad (A-7)\]

\[-2 \sum_{a,b,c,i,j,k} \frac{< ak | ij > < cj | ab > (< ic | λ > < kb | µ > + < kb | λ > < ic | µ >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_b)} \quad (A-8)\]

\[(VC1 - 6) + (VC2 - 5) = 4 \sum_{a,b,c,d,i,j} \frac{< ab | dj > < cj | ab > < ic | λ > < id | µ >}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_i - \varepsilon_d)} \quad (A-9)\]

\[(VC1 - 7) + (VC2 - 8) = -4 \sum_{a,b,c,i,j,k} \frac{< kb | ij > < cj | ab > (< ic | λ > < ka | µ > + < ka | λ > < ic | µ >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_a)} \quad (A-10)\]

\[(VC1 - 9) + (VC1 - 10) = -4 \sum_{a,b,c,i,j,k} \frac{< ab | ij > < cj | ab > (< ik | λ > < kc | µ > + < kc | λ > < ik | µ >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_c)} \quad (A-11)\]

\[(VC1 - 11) + (VC3 - 7) = -4 \sum_{a,b,c,i,j,k} \frac{< ab | ij > < cj | ab > (< ik | λ > < kc | µ > + < kc | λ > < ik | µ >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_c)} \quad (A-12)\]

\[(VC1 - 12) + (VC4 - 8) = 4 \sum_{a,b,c,d,i,j} \frac{< ab | ij > < cj | db > (< ic | λ > < da | µ > + < ic | µ > < da | λ >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_d - \varepsilon_b)(\varepsilon_i - \varepsilon_c)} \quad (A-13)\]
\[ \sum_{a,b,c,d,i,j} <ab|ij><cj|ab> \left( <id\lambda><dc\mu> + <id\mu><dc\lambda> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_d)(\varepsilon_i - \varepsilon_c) \]
\[ (VC1 - 13) + (VC1 - 14) = \]

\[ -4 \sum_{a,b,c,i,j,k} <ab|ij><cj|kb> \left( <ic\lambda><ka\mu> + <ka\lambda><ic\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_a) \]
\[ (VC1 - 15) + (VC2 - 15) = \]

\[ -4 \sum_{a,b,c,i,j,k} <ab|ij><kj|ab> \left( <ak\lambda><bl\mu> + <jl\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_l - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a) \]
\[ (VC1 - 16) = \]

\[ 2 \sum_{a,b,i,j,k,l} <ab|ij><ij|kl> \left( <ak\lambda><bl\mu> + <jl\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_l - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a) \]
\[ (VC2 - 1) = \]

\[ 2 \sum_{a,b,c,i,j,k,l} <ac|ij><ij|kb> \left( <ak\lambda><bc\mu> + <bc\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_k - \varepsilon_a) \]
\[ (VC2 - 3) + (VC3 - 2) = \]

\[ 2 \sum_{a,b,i,j,k,l} <al|ij><ij|kb> \left( <ak\lambda><bl\mu> + <jl\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_b) \]
\[ (VC2 - 4) + (VC4 - 2) = \]

\[ -2 \sum_{a,b,c,i,j,k} <ac|ij><ij|kb> \left( <ak\lambda><bc\mu> + <bc\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_k - \varepsilon_a) \]
\[ (VC2 - 6) = \]

\[ 2 \sum_{a,b,i,j,k,l} <al|ij><ij|kb> \left( <ak\lambda><bl\mu> + <jl\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_b) \]
\[ (VC2 - 7) = \]

\[ 4 \sum_{a,b,i,j,k,l} <lb|ij><ij|kb> \left( <ak\lambda><al\mu> + <jl\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_a) \]
\[ (VC2 - 4) + (VC4 - 2) = \]

\[ (VC2 - 6) = \]

\[ 2 \sum_{a,b,i,j,k,l} <al|ij><ij|kb> \left( <ak\lambda><bl\mu> + <jl\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_b) \]
\[ (VC2 - 7) = \]

\[ 4 \sum_{a,b,i,j,k,l} <lb|ij><ij|kb> \left( <ak\lambda><al\mu> + <jl\lambda><ak\mu> \right) \]
\[ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_a) \]
\[ (VC2 - 4) + (VC4 - 2) = \]
\[
(VC2 - 9) + (VC2 - 10) = -4 \sum_{a,b,c,i,j,k} \frac{< ab|ij > < ij|kb > (< ck\lambda > < ac\mu > + < ac\lambda > < ck\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_c)(\varepsilon_k - \varepsilon_a)} \\

(VC2 - 11) + (VC4 - 7) = -4 \sum_{a,b,c,i,j,k} \frac{< ab|ij > < ij|kb > (< ck\lambda > < ac\mu > + < ac\lambda > < ck\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_b - \varepsilon_c)(\varepsilon_k - \varepsilon_c)} \\

(VC2 - 12) + (VC3 - 8) = 4 \sum_{a,b,i,j,k,l} \frac{< ab|ij > < lj|kb > (< ak\lambda > < il\mu > + < il\lambda > < ak\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_l + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)} \\

(VC2 - 13) + (VC2 - 14) = 4 \sum_{a,b,i,j,k,l} \frac{< ab|ij > < ij|kb > (< al\lambda > < lk\mu > + < al\mu > < lk\lambda >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_a)} \\

(VC2 - 16) = -4 \sum_{a,b,c,i,j,k} \frac{< ab|ij > < ij|cb > < ak\lambda > < ck\mu >}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_k - \varepsilon_c)} \\

(VC3 - 3) + (VC3 - 5) = \sum_{a,b,i,j,k,l} \frac{< ab|ik > < lj|ab > (< jk\lambda > < il\mu > + < jk\mu > < il\lambda >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_l + \varepsilon_j - \varepsilon_a - \varepsilon_b)} \\

(VC3 - 4) + (VC4 - 5) = - \sum_{a,b,c,i,j,k} \frac{< ab|ik > < ij|cb > (< jk\lambda > < ac\mu > + < ac\lambda > < jk\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_b - \varepsilon_c)} \\

(VC3 - 6) + (VC4 - 3) = - \sum_{a,b,c,i,j,k} \frac{< ab|ik > < ij|cb > (< jk\lambda > < ac\mu > + < ac\lambda > < jk\mu >)}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_c - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_c - \varepsilon_b)}
\]
\[ (VC3 - 9) + (VC - 10) = \]
\[ 2 \sum_{a,b,i,j,k,l} \frac{< ab|ik > < ij|ab > (< jl|lk > + < jk|lk >)}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_l - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)} \]  
\[ (A-30) \]

\[ (VC3 - 11) + (VC4 - 12) = \]
\[ -2 \sum_{a,b,c,i,j,k} \frac{< ab|ik > < ij|ac > (< jk|bc > + < bc|\lambda >)}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)} \]  
\[ (A-31) \]

\[ (VC3 - 12) + (VC4 - 11) = \]
\[ -2 \sum_{a,b,c,i,j,k} \frac{< ab|ik > < ij|ac > (< jk|bc > + < bc|\lambda >)}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)} \]  
\[ (A-32) \]

\[ (VC3 - 13) + (VC3 - 14) = \]
\[ -4 \sum_{a,b,c,i,j,k} \frac{< ab|ik > < ij|ab > < jk|\lambda > < kc|\mu >}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)} \]  
\[ (A-33) \]

\[ (VC4 - 4) + (VC4 - 6) = \]
\[ \sum_{a,b,c,d,i,j} \frac{< ac|ij > < ij|db > (< cb|\lambda > < ad|\mu > + < ad|\lambda > < cb|\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)} \]  
\[ (A-34) \]

\[ (VC4 - 9) + (VC4 - 10) = \]
\[ 2 \sum_{a,b,c,d,i,j} \frac{< ac|ij > < ij|ad > (< cb|\lambda > < bd|\mu > + < cb|\lambda > < bd|\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)} \]  
\[ (A-35) \]

\[ (VC4 - 13) + (VC4 - 14) = \]
\[ -4 \sum_{a,b,c,i,j,k} \frac{< ac|ij > < ij|ab > < bk|\lambda > < kc|\mu >}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_c)} \]  
\[ (A-36) \]

\[ (VC5 - 1) + (VC6 - 1) = \]
\[ 2 \sum_{a,b,c,i,j,k} \frac{< ab|ij > < cj|bk > (< ic|\lambda > < ak|\mu > + < ic|\mu > < ak|\lambda >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_a)} \]  
\[ (A-37) \]
\[ (VC5 - 2) = -2 \sum_{a,b,c,d,i,j} \frac{< ab|ij > < cd|ba > < ic\lambda > < dj\mu >}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_j - \varepsilon_d)} \]  
(A–38)

\[ (VC5 - 3) + (VC8 - 1) = 2 \sum_{a,b,c,i,j,k} \frac{< ab|ik > < cj|ba > ( < ic\lambda > < jk\mu > + < ic\mu > < jk\lambda >) }{ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c) } \]  
(A–39)

\[ (VC5 - 4) + (VC7 - 12) = -2 \sum_{a,b,c,d,i,j} \frac{ < db|ij > < cj|ba > ( < ic\lambda > < da\mu > + < da\lambda > < ic\mu > ) }{ (\varepsilon_i + \varepsilon_j - \varepsilon_d - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c) } \]  
(A–40)

\[ (VC5 - 5) + (VC7 - 8) = -2 \sum_{a,b,c,d,i,j} \frac{ < ab|ij > < cj|da > ( < ic\lambda > < db\mu > + < db\lambda > < ic\mu > ) }{ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_d)(\varepsilon_i - \varepsilon_c) } \]  
(A–41)

\[ (VC5 - 6) + (VC6 - 8) = 2 \sum_{a,b,c,i,j,k} \frac{ < ak|ij > < cj|ba > ( < ic\lambda > < kb\mu > + < ic\mu > < kb\lambda > ) }{ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_b) } \]  
(A–42)

\[ (VC5 - 7) = -2 \sum_{a,b,c,d,i,j} \frac{ < ab|id > < cj|ba > < ic\lambda > < jb\mu > }{ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_j - \varepsilon_d) } \]  
(A–43)

\[ (VC5 - 8) + (VC6 - 6) = 2 \sum_{a,b,c,i,j,k} \frac{ < kb|ij > < cj|ba > ( < ic\lambda > < ka\mu > + < ic\mu > < ka\lambda > ) }{ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_a) } \]  
(A–44)

\[ (VC5 - 9) = -2 \sum_{a,b,c,d,i,j} \frac{ < ab|dj > < cj|ba > < ic\lambda > < id\mu > }{ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_i - \varepsilon_d) } \]  
(A–45)

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\[ (VC_5 - 10) + (VC_8 - 10) = \]
\[ 2 \sum_{a,b,c,i,j,k} \frac{<ab|kj><cj|ba> (\langle ic\lambda >\langle ik\mu > + \langle ic\mu >\langle ik\lambda >)}{(\varepsilon_k + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)} \]  
(A–46)

\[ (VC_5 - 11) + (VC_5 - 12) = \]
\[ 2 \sum_{a,b,c,i,j,k} \frac{<ab|kj><cj|ba> (\langle ic\lambda >\langle ik\mu > + \langle ic\mu >\langle ik\lambda >)}{(\varepsilon_k + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_i - \varepsilon_c)} \]  
(A–47)

\[ (VC_5 - 13) + (VC_5 - 14) = \]
\[ -2 \sum_{a,b,c,d,i,j} \frac{<ab|ij><cj|ba> (\langle id\lambda >\langle dc\mu > + \langle dc\lambda >\langle id\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_i - \varepsilon_d)} \]  
(A–48)

\[ (VC_5 - 15) + (VC_6 - 15) = \]
\[ 2 \sum_{a,b,c,i,j,k} \frac{<ab|ij><cj|ka> (\langle ic\lambda >\langle bk\mu > + \langle ic\mu >\langle bk\lambda >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_b)} \]  
(A–49)

\[ (VC_5 - 16) = \]
\[ 2 \sum_{a,b,c,i,j,k} \frac{<ab|ij><kj|ba> (\langle ic\lambda >\langle ck\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i - \varepsilon_c)(\varepsilon_k - \varepsilon_c)} \]  
(A–50)

\[ (VC_6 - 2) = \]
\[ -2 \sum_{a,b,i,j,k,l} \frac{<ab|ij><ji|kl> (\langle ak\lambda >\langle lb\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_b)} \]  
(A–51)

\[ (VC_6 - 3) + (VC_7 - 1) = \]
\[ 2 \sum_{a,b,c,i,j,k} \frac{<ac|ij><ji|kb> (\langle ak\lambda >\langle cb\mu > + \langle ak\mu >\langle cb\lambda >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_k - \varepsilon_a)} \]  
(A–52)

\[ (VC_6 - 4) + (VC_8 - 8) = \]
\[ -2 \sum_{a,b,i,j,k,l} \frac{<ab|ij><jl|kb> (\langle ak\lambda >\langle il\mu > + \langle il\lambda >\langle ak\mu >)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)} \]  
(A–53)
\[-2 \sum_{a,b,i,j,k,l} \langle ab|ij \rangle < li|kb \rangle \langle ak \lambda > < j l \mu > + \langle jl|\lambda > < ak\mu > \rangle \]

\[
\frac{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_l - \varepsilon_a)(\varepsilon_k - \varepsilon_a)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_l - \varepsilon_a)(\varepsilon_k - \varepsilon_a)}
\]

(A-54)

\[
(VC6 - 7) = \]

\[-2 \sum_{a,b,i,j,k,l} \langle al|ij \rangle < ji|kb \rangle < ak \lambda > < lb \mu > \]

\[
\frac{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_a)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_a)}
\]

(A-55)

\[
(VC6 - 9) = \]

\[-2 \sum_{a,b,i,j,k,l} \langle lb|ij \rangle < ji|kb \rangle < ak \lambda > < la \mu > \]

\[
\frac{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_a)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_l - \varepsilon_a)}
\]

(A-56)

\[
(VC6 - 10) + (VC7 - 9) = \]

\[2 \sum_{a,b,c,i,j,k} \langle ab|ij \rangle < ji|kb \rangle \langle ck \lambda > < ac \mu > + \langle ck \mu > < ac \lambda > \rangle \]

\[
\frac{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_c - \varepsilon_b)(\varepsilon_k - \varepsilon_c)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_c - \varepsilon_b)(\varepsilon_k - \varepsilon_c)}
\]

(A-57)

\[
(VC6 - 11) + (VC6 - 12) = \]

\[2 \sum_{a,b,c,i,j,k} \langle cb|ij \rangle < ji|kb \rangle \langle ak \lambda > < ac \mu > + \langle ak \mu > < ac \lambda > \rangle \]

\[
\frac{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_k - \varepsilon_c)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_k - \varepsilon_c)}
\]

(A-58)

\[
(VC6 - 13) + (VC6 - 14) = \]

\[-2 \sum_{a,b,i,j,k,l} \langle ab|ij \rangle < ji|kb \rangle \langle kl \lambda > < al \mu > + \langle al \lambda > < kl \mu > \rangle \]

\[
\frac{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_k - \varepsilon_a)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_k - \varepsilon_a)}
\]

(A-59)

\[
(VC6 - 16) = \]

\[2 \sum_{a,b,c,i,j,k} \langle ab|ij \rangle < ji|cb \rangle < ak \lambda > < kc \mu > \]

\[
\frac{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_k - \varepsilon_c)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k - \varepsilon_a)(\varepsilon_k - \varepsilon_c)}
\]

(A-60)

\[
(VC7 - 2) + (VC7 - 3) = \]

\[- \sum_{a,b,c,d,i,j} \langle ac|ij \rangle < ji|db \rangle \langle bc \lambda > < ad \mu > + \langle ad \lambda > < bc \mu > \rangle \]

\[
\frac{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_d - \varepsilon_b)}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_d - \varepsilon_b)}
\]

(A-61)
\[
\sum_{a,b,c,i,j,k} < ac|ij > < ki|ab > \frac{1}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)}
\] (A–62)

\[
(VC7 - 4) + (VC8 - 5) =
\]

\[
\sum_{a,b,c,i,j,k} < ac|ij > < ki|ab > \frac{1}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)}
\] (A–63)

\[
(VC7 - 5) + (VC8 - 6) =
\]

\[
\sum_{a,b,c,i,j,k} < ac|ij > < jk|ab > \frac{1}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_c)(\varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b)}
\] (A–64)

\[
(VC7 - 6) + (VC8 - 7) =
\]

\[
\sum_{a,b,c,i,j,k} < ac|ij > < jk|ab > \frac{1}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b)}
\] (A–65)

\[
(VC7 - 7) + (VC8 - 4) =
\]

\[
\sum_{a,b,c,d,i,j} < ac|ij > < ji|ad > \frac{1}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_d)}
\] (A–66)

\[
(VC7 - 10) + (VC7 - 11) =
\]

\[
\sum_{a,b,c,i,j} < ac|ij > < ji|ad > \frac{1}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_d)}
\] (A–67)

\[
2 \sum_{a,b,c,i,j,k} < ac|ij > < ji|ab > < bk|cl > \frac{1}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_c)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k + \varepsilon_c)}
\] (A–68)

\[
(VC8 - 13) + (VC8 - 14) =
\]

\[
\sum_{a,b,c,i,j,k,l} < ab|ik > < lj|ba > \frac{1}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_l + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)}
\] (A–69)
\[ (VC8 - 13) + (VC8 - 14) = \]
\[
2 \sum_{a,b,c,i,j,k} <ab|ik><ij|ba><ck|\lambda><cj|\mu> \\
\frac{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_j - \varepsilon_c)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_a)
\]  

\[ (VC9 - 1) + (VC11 - 8) = \]
\[
2 \sum_{i,j,k,a,b} f_{ia} f_{kj} (<ij|\lambda><ak|\mu>+<ak|\lambda><ij|\mu>) \\
\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_a)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_b)
\]  

\[ (VC9 - 2) + (VC10 - 3) = \]
\[
- \sum_{i,j,a,b} f_{ia} f_{bj} (<ij|\lambda><ab|\mu>+<ab|\lambda><ij|\mu>) \\
\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_b)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_b)
\]  

\[ (VC9 - 3) + (VC10 - 2) = \]
\[
- \sum_{i,j,a,b} f_{ia} f_{bj} (<ij|\lambda><ab|\mu>+<ab|\lambda><ij|\mu>) \\
\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_b)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_b)
\]  

\[ (VC9 - 4) + (VC12 - 5) = \]
\[
-2 \sum_{i,j,a,b} f_{ia} f_{j\lambda} (b|ib>\mu>+b|\mu>b|ib>) \\
\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_b)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_b)
\]  

\[ (VC9 - 5) + (VC9 - 6) = \]
\[
\sum_{i,j,k,a} f_{ia} f_{ka} (<ij|\lambda><kj|\mu>+<kj|\lambda><ij|\mu>) \\
\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_a)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_a)
\]  

\[ (VC9 - 7) = \]
\[
-2 \sum_{i,j,a,b} f_{ia} f_{aj} <ib|\lambda><j|b\mu> \\
\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_b)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_b)
\]  

\[ (VC9 - 8) + (VC15 - 3) = \]
\[
-4 \sum_{i,j,k,a,b} f_{ia} <jb|ak> (i|j\lambda><k|b\mu>+k|b\lambda><i|j\mu>) \\
\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_b)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_b)
\]
\[(VC9 - 9) + (VC14 - 4) = \]
\[2 \sum_{i,j,k,a,b} f_{aj} < ab|ki > ( < ij\lambda > < kb\mu > + < kb\lambda > < ij\mu >) \]
\[\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_b)}{\varepsilon_i - \varepsilon_a}(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_b)\] (A–78)

\[(VC9 - 10) + (VC13 - 10) = \]
\[2 \sum_{i,j,k,a,b} f_{ai} < bj|ak > ( < ij\lambda > < kb\mu > + < kb\lambda > < ij\mu >) \]
\[\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_b)}{\varepsilon_i - \varepsilon_a}(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_b)\] (A–79)

\[(VC10 - 1) + (VC12 - 7) = \]
\[2 \sum_{i,a,b,c} f_{bi} f_{ac} (< ab\lambda > < ic\mu > + < ic\lambda > < ab\mu >) \]
\[\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_c)}{\varepsilon_i - \varepsilon_a}(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_b)\] (A–80)

\[(VC10 - 4) + (VC11 - 5) = \]
\[-2 \sum_{i,j,a,b} f_{ib} f_{ij} (< ab\lambda > < aj\mu > + < aj\lambda > < ab\mu >) \]
\[\frac{(\varepsilon_j - \varepsilon_a)(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)}{\varepsilon_j - \varepsilon_a}(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_b)\] (A–81)

\[(VC10 - 5) + (VC10 - 6) = \]
\[\sum_{i,a,b,c} f_{bi} f_{ic} (< ab\lambda > < ac\mu > + < ac\lambda > < ab\mu >) \]
\[\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_c)}{\varepsilon_i - \varepsilon_a}(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_c)\] (A–82)

\[(VC10 - 7) = \]
\[-2 \sum_{i,j,a,b} f_{ia} f_{ib} (< bj\lambda > < aj\mu > + < aj\lambda > < bj\mu >) \]
\[\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_a)}{\varepsilon_i - \varepsilon_a}(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_a)\] (A–83)

\[(VC10 - 8) + (VC15 - 4) = \]
\[4 \sum_{i,j,a,b,c} f_{ib} < ic|aj > (< ab\lambda > < cj\mu > + < cj\lambda > < ab\mu >) \]
\[\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_c)}{\varepsilon_i - \varepsilon_a}(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_c)\] (A–84)

\[(VC10 - 9) + (VC14 - 2) = \]
\[-2 \sum_{i,j,a,b,c} f_{ib} < ca|ij > (< ab\lambda > < cj\mu > + < cj\lambda > < ab\mu >) \]
\[\frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_c)}{\varepsilon_i - \varepsilon_a}(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_c)\] (A–85)
\[-2 \sum_{i,j,a,b,c} f_{bc} <ic|ja> ( <ab\lambda><cj\mu> + <cj\lambda><ab\mu> ) / (\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_c) \] (A-86)

\[(VC10 - 10) + (VC13 - 9) = \]

\[2 \sum_{i,j,k,a} f_{ij} f_{aj} (<ak\lambda><ik\mu> + <ik\lambda><ak\mu> ) / (\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_b)(\varepsilon_k - \varepsilon_a) \] (A-87)

\[(VC11 - 1) + (VC11 - 2) = \]

\[-2 \sum_{i,j,a,b} f_{ij} f_{aj} (<ab\lambda><ib\mu> + <ib\lambda><ab\mu> ) / (\varepsilon_j - \varepsilon_a)(\varepsilon_i - \varepsilon_b) \] (A-88)

\[(VC11 - 3) + (VC11 - 4) = \]

\[2 \sum_{i,j,k,a} f_{jk} f_{ki} (<aj\lambda><ai\mu> + <ai\lambda><aj\mu> ) / (\varepsilon_i - \varepsilon_a)(\varepsilon_k - \varepsilon_a)(\varepsilon_j - \varepsilon_a) \] (A-89)

\[(VC11 - 6) = \]

\[-2 \sum_{i,j,a,b} f_{ij} f_{ab} (<bj\lambda><ai\mu> + <ai\lambda><bj\mu> ) / (\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_b)(\varepsilon_i - \varepsilon_b) \] (A-90)

\[(VC11 - 7) + (VC12 - 8) = \]

\[-2 \sum_{i,j,a,b} f_{ai} f_{jb} (<aj\lambda><bi\mu> + <bi\lambda><aj\mu> ) / (\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_i - \varepsilon_b) \] (A-91)

\[(VC11 - 9) + (VC12 - 9) = \]

\[-2 \sum_{i,j,a,b} f_{ai} f_{ib} (<aj\lambda><bj\mu> ) / (\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_j - \varepsilon_b) \] (A-92)

\[(VC11 - 10) = \]

\[-4 \sum_{i,j,k,a,b} f_{ia} <ib|jk> ( <aj\lambda><kb\mu> + <kb\lambda><aj\mu> ) / (\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_b) \] (A-93)

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\begin{align}
(VC11 - 12) + (VC15 - 2) = & \sum_{i,j,k,a,b} f_{ij} \langle ab|ik \rangle (\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_a) (\varepsilon_k - \varepsilon_b) \\
(VC11 - 13) + (VC13 - 11) = & \sum_{i,j,k,a,b} f_{ij} \langle ak|bi \rangle (\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_a) (\varepsilon_k - \varepsilon_b) \\
(VC11 - 14) + (VC14 - 3) = & \sum_{i,j,k,a,b} f_{ij} \langle ab|ki \rangle (\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_a) (\varepsilon_k - \varepsilon_b) \\
(VC11 - 15) + (VC14 - 5) = & \sum_{i,j,k,a,b} f_{ai} \langle kij \rangle (\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_a) (\varepsilon_k - \varepsilon_b) \\
(VC11 - 16) + (VC13 - 7) = & \sum_{i,j,k,a,b} f_{ai} \langle bijk \rangle (\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_a) (\varepsilon_k - \varepsilon_b) \\
(VC12 - 1) + (VC12 - 2) = & \sum_{a,b,c,i} f_{ab} f_{ib} \langle ac\lambda \langle ic\mu \rangle + \langle ic\lambda \langle ac\mu \rangle \rangle \rangle (\varepsilon_i - \varepsilon_a) (\varepsilon_i - \varepsilon_b) (\varepsilon_i - \varepsilon_c) \\
(VC12 - 3) + (VC12 - 4) = & \sum_{i,j,a,b} f_{ib} f_{ab} \langle ij\lambda \langle aj\mu \rangle + \langle aj\lambda \langle ij\mu \rangle \rangle \rangle (\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_a) \\
(VC12 - 6) = & \sum_{a,b,c,i} f_{ab} f_{ac} \langle ib\lambda \langle ic\mu \rangle \rangle (\varepsilon_i - \varepsilon_a) (\varepsilon_i - \varepsilon_b) (\varepsilon_i - \varepsilon_c)
\end{align}
(VC12 − 10) =
\[-2 \sum_{i,j,a,b} f_{ib}f_{bj} \frac{< ia\lambda > < ja\mu >}{(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)}\]  

(A–102)

(VC12 − 11) + (VC15 − 6) =
\[4 \sum_{a,b,c,i,j} f_{ib} ac bj \frac{(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_c)}{< ia\lambda > < cj\mu > + < cj\lambda > < ia\mu >}\]  

(A–103)

(VC12 − 12) + (VC15 − 1) =
\[4 \sum_{a,b,c,i,j} f_{ab} bc ij \frac{(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_c)}{< ia\lambda > < cj\mu > + < cj\lambda > < ia\mu >}\]  

(A–104)

(VC12 − 13) + (VC13 − 12) =
\[-2 \sum_{a,b,c,i,j} f_{ab} ji ic \frac{(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_c)}{< ia\lambda > < cj\mu > + < cj\lambda > < ia\mu >}\]  

(A–105)

(VC12 − 14) + (VC14 − 1) =
\[-2 \sum_{a,b,c,i,j} f_{ab} cj ij \frac{(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_c)}{< ia\lambda > < cj\mu > + < cj\lambda > < ia\mu >}\]  

(A–106)

(VC12 − 15) + (VC14 − 10) =
\[-2 \sum_{a,b,c,i,j} f_{ia} bj ca \frac{(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_c)}{< ib\lambda > < cj\mu > + < cj\lambda > < ib\mu >}\]  

(A–107)

(VC12 − 16) + (VC13 − 8) =
\[-2 \sum_{a,b,c,i,j} f_{ia} bc ja \frac{(\varepsilon_i - \varepsilon_b)(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_c)}{< ib\lambda > < cj\mu > + < cj\lambda > < ib\mu >}\]  

(A–108)

(VC13 − 1) + (VC13 − 2) =
\[2 \sum_{i,j,k,a,b} f_{ai} bi aj \frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_b)(\varepsilon_k - \varepsilon_b)}{< bk\lambda > < kj\mu > + < kj\lambda > < bk\mu >}\]  

(A–109)
\[
-2 \sum_{a,b,c,i,j} f_{ai} < bi|aj > (\langle c_j \lambda > b_c \mu > + \langle b_c \lambda > c_j \mu >) \\
(\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_b) (\varepsilon_j - \varepsilon_c)
\]
(A-110)

\[
(VC13 - 5) + (VC14 - 9) =

2 \sum_{i,j,k,a,b} f_{ai} < ki|aj > (\langle b_j \lambda > b_k \mu > + \langle b_k \lambda > b_j \mu >) \\
(\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_b) (\varepsilon_k - \varepsilon_b)
\]
(A-111)

\[
(VC13 - 6) + (VC14 - 6) =

-2 \sum_{a,b,c,i,j} f_{ai} < bi|ac > (\langle c_j \lambda > b_j \mu > + \langle b_j \lambda > c_j \mu >) \\
(\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_b) (\varepsilon_j - \varepsilon_c)
\]
(A-112)

\[
(VC13 - 13) + (VC15 - 14) =

-4 \sum_{a,b,c,i,j,k} < ac|ik > < bi|aj > (\langle b_j \lambda > c_k \mu > + \langle c_k \lambda > b_j \mu >) \\
(\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_b) (\varepsilon_k - \varepsilon_c)
\]
(A-113)

\[
(VC13 - 14) =

2 \sum_{a,b,c,i,j,k} < ak|ci > < bi|aj > < b_j \lambda > c_k \mu > \\
(\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_b) (\varepsilon_k - \varepsilon_c)
\]
(A-114)

\[
(VC13 - 15) + (VC14 - 14) =

2 \sum_{a,b,c,i,j,k} < ac|ki > < bi|aj > (\langle b_j \lambda > c_k \mu > + \langle c_k \lambda > b_j \mu >) \\
(\varepsilon_i - \varepsilon_a) (\varepsilon_j - \varepsilon_b) (\varepsilon_k - \varepsilon_c)
\]
(A-115)

\[
(VC14 - 7) + (VC14 - 8) =

2 \sum_{i,j,k,a,b} f_{aj} < ab|ij > (\langle b_k \lambda > i_k \mu > + \langle i_k \lambda > b_k \mu >) \\
(\varepsilon_j - \varepsilon_a) (\varepsilon_i - \varepsilon_b) (\varepsilon_k - \varepsilon_b)
\]
(A-116)

\[
(VC14 - 11) + (VC14 - 12) =

-2 \sum_{a,b,c,i,j} f_{aj} < ab|ij > (\langle i_c \lambda > b_c \mu > + \langle b_c \lambda > i_c \mu >) \\
(\varepsilon_j - \varepsilon_a) (\varepsilon_i - \varepsilon_b) (\varepsilon_i - \varepsilon_c)
\]
(A-117)
\[ (VC14 - 13) + (VC15 - 15) = -4 \sum_{a,b,c,i,j,k}^{<cj|ka><ab|ij> - (ib\lambda><ck\mu> + <ck\lambda><ib\mu>)}{(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_c)} \]

\[ (VC14 - 15) = 2 \sum_{a,b,c,i,j,k}^{<ab|ji><ki|ac><jb\lambda><ck\mu>}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_b)(\varepsilon_k - \varepsilon_c)} \]

\[ (VC15 - 7) - (VC15 - 8) = -8 \sum_{i,j,k,a,b}^{f_{ai}<ab|ij> - (bk\lambda><jk\mu> + jk\lambda><bk\mu>)}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_b)(\varepsilon_k - \varepsilon_b)} \]

\[ (VC15 - 9) + (VC15 - 10) = 8 \sum_{a,b,c,i,j}^{f_{ai}<ab|ij> - (cj\lambda><bc\mu> + bc\lambda><cj\mu>)}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_c)(\varepsilon_j - \varepsilon_b)} \]

\[ (VC15 - 11) = -8 \sum_{i,j,k,a,b}^{f_{ai}<ak|ij><jb\lambda><kb\mu>}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_b)(\varepsilon_k - \varepsilon_b)} \]

\[ (VC15 - 12) = 8 \sum_{a,b,c,i,j}^{f_{ai}<ab|ic><bj\lambda><cj\mu>}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_b)(\varepsilon_j - \varepsilon_c)} \]

\[ (VC15 - 13) = 16 \sum_{a,b,c,i,j}^{<ab|ij><ci|ka><bj\lambda><ck\mu>}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_b)(\varepsilon_k - \varepsilon_c)} \]

\[ (V1) + (V2) = -2 \sum_{i,a,b}^{<i|V_{c}|a> - (ab\lambda><ib\mu> + ib\lambda><ab\mu>)}{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)} \]
\[(V3) + (V4) = 2 \sum_{i,j,a}^{\text{c}} < i|V_c|a > (\langle aj\lambda \rangle \langle ij\mu \rangle + \langle ij\lambda \rangle \langle aj\mu \rangle) \frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)}{\varepsilon_j^2 - \varepsilon_a^2} \] (A–126)

\[(VC5) = 2 \sum_{i,j,a}^{\text{c}} < i|V_c|j > \langle ai\lambda \rangle \langle aj\mu \rangle \frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)}{\varepsilon_j^2 - \varepsilon_a^2} \] (A–127)

\[(VC6) = -2 \sum_{i,a,b}^{\text{c}} < a|V_c|b > \langle ai\lambda \rangle \langle bj\mu \rangle \frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)}{\varepsilon_i^2 - \varepsilon_a^2} \] (A–128)
APPENDIX B
INTERPRETATION OF DIAGRAMS OF EXACT-EXCHANGE SECOND KERNEL

For the calculation of last term in equation (6–5) an auxiliary basis set decomposition is used

$$< \varphi_a \varphi_b \varphi_c \varphi_d | g_{\sigma \sigma} | \varphi_{i \sigma} \varphi_{j \sigma} \varphi_{k \sigma} > = \sum_{\lambda, \mu, \nu} < \varphi_a \varphi_i \varphi_{j \sigma} \varphi_{k \sigma} | g_{\sigma \sigma} | \varphi_{i \sigma} \varphi_{j \sigma} \varphi_{k \sigma} > g_{\lambda \mu \nu} \quad (B-1)$$

where $\chi_{\eta}$ are the auxiliary functions. The expression for $g_{\lambda \mu \nu}$ can be written in the form (B–2)

$$g_{\lambda \mu \nu} = \sum_{\kappa, \eta, \zeta} (X^{-1})_{\lambda \kappa} (X^{-1})_{\mu \eta} (X^{-1})_{\nu \zeta} \Xi_{\kappa \eta \zeta} + \sum_{\kappa, \eta} (X^{-1})_{\lambda \kappa} (X^{-1})_{\mu \eta} \Theta_{\kappa \eta \zeta} + \sum_{\kappa, \eta} (X^{-1})_{\mu \kappa} (X^{-1})_{\nu \eta} \Theta_{\kappa \eta \zeta} \quad (B-2)$$

where

$$X_{\lambda \mu} = 2 \sum_{a,i} \frac{< \varphi_{a \sigma} \varphi_{i \sigma} \lambda > < \varphi_{a \sigma} \varphi_{i \sigma} \mu >}{\varepsilon_i - \varepsilon_a} \quad (B-3)$$

Two separate $g_{\lambda \mu \nu}$ should be constructed for each spin component. Expressions for $\Theta_{\kappa \eta \zeta}$, $\Theta_{\lambda \kappa \eta}$ and $\Theta_{\mu \kappa \eta}$ can be written in terms of the diagrams (F1) - (F18).

$$\Theta_{\nu \kappa \eta} = 2 \sum_{i,j,a} f_{i\alpha} \left( \frac{< \varphi_{a \sigma} \varphi_{j \sigma} \kappa > < \varphi_{i \sigma} \varphi_{j \sigma} \eta >}{\varepsilon_i - \varepsilon_a} \right) - 2 \sum_{i,a,b} f_{i\alpha} \left( \frac{< \varphi_{i \sigma} \varphi_{b \sigma} \kappa > < \varphi_{i \sigma} \varphi_{b \sigma} \eta >}{\varepsilon_i - \varepsilon_a} \right) + 2 \sum_{i,j,a} f_{ij} \left( \frac{< \varphi_{a \sigma} \varphi_{i \sigma} \kappa > < \varphi_{a \sigma} \varphi_{j \sigma} \eta >}{\varepsilon_i - \varepsilon_a} \right) - 2 \sum_{i,a,b} f_{i\alpha} \left( \frac{< \varphi_{i \sigma} \varphi_{b \sigma} \kappa > < \varphi_{i \sigma} \varphi_{b \sigma} \eta >}{\varepsilon_i - \varepsilon_a} \right) \quad (B-4)$$

where the integrals involving the exchange kernel can be calculated using the formula

$$f_{pq\nu} = \sum_{\kappa \lambda \mu} < \varphi_{p \sigma} \varphi_{q \sigma} \kappa > (X^{-1})_{\lambda \kappa} Q_{\lambda \mu} (X^{-1})_{\mu \nu} \quad (B-5)$$
Algebraic expression for $\Xi_{\kappa \eta \zeta}$ consist of two parts. The first part is represented by the sum of diagrams (VX1) - (VX8) and (SX7) - (SX14).

$$D1 = -2 \sum_{a,b,c,i} \left( \langle \varphi_i | V_x | \varphi_a \rangle + K_{ia} \right) * F1$$

$$F1 = \left( \langle \varphi_i \varphi_c \kappa \rangle \langle \varphi_b \varphi_d \eta \rangle \langle \varphi_a \varphi_b \zeta \rangle + \langle \varphi_i \varphi_c \kappa \rangle \langle \varphi_b \varphi_c \zeta \rangle \langle \varphi_a \varphi_d \eta \rangle \right) +$$

$$\langle \varphi_i \varphi_c \zeta \rangle \langle \varphi_b \varphi_d \eta \rangle \langle \varphi_a \varphi_b \kappa \rangle + \langle \varphi_i \varphi_c \eta \rangle \langle \varphi_b \varphi_c \kappa \rangle \langle \varphi_a \varphi_d \zeta \rangle +$$

$$\langle \varphi_i \varphi_c \zeta \rangle \langle \varphi_b \varphi_c \kappa \rangle \langle \varphi_a \varphi_d \eta \rangle + \langle \varphi_i \varphi_c \eta \rangle \langle \varphi_b \varphi_c \zeta \rangle \langle \varphi_a \varphi_b \kappa \rangle \right) \quad (B-6)$$

$$D2 = -2 \sum_{i,j,k,a} \left( \langle \varphi_i | V_x | \varphi_a \rangle + K_{ia} \right) * F2$$

$$F2 = \left( \langle \varphi_a \varphi_k \kappa \rangle \langle \varphi_k \varphi_j \eta \rangle \langle \varphi_i \varphi_j \zeta \rangle + \langle \varphi_a \varphi_k \kappa \rangle \langle \varphi_k \varphi_j \zeta \rangle \langle \varphi_i \varphi_j \eta \rangle \right) +$$

$$\langle \varphi_a \varphi_k \zeta \rangle \langle \varphi_k \varphi_j \eta \rangle \langle \varphi_i \varphi_j \kappa \rangle + \langle \varphi_a \varphi_k \eta \rangle \langle \varphi_k \varphi_j \kappa \rangle \langle \varphi_i \varphi_j \zeta \rangle +$$

$$\langle \varphi_a \varphi_k \zeta \rangle \langle \varphi_k \varphi_j \kappa \rangle \langle \varphi_i \varphi_j \eta \rangle + \langle \varphi_a \varphi \eta \rangle \langle \varphi_k \varphi_j \zeta \rangle \langle \varphi_i \varphi_j \kappa \rangle \right) \quad (B-7)$$

$$D3 = 2 \sum_{i,j,a,b} \left( \langle \varphi_i | V_x | \varphi_a \rangle + K_{ia} \right) * F3$$

$$F3 = \left( \langle \varphi_i \varphi_j \kappa \rangle \langle \varphi_j \varphi_b \eta \rangle \langle \varphi_a \varphi_b \zeta \rangle + \langle \varphi_i \varphi_j \kappa \rangle \langle \varphi_j \varphi_b \zeta \rangle \langle \varphi_a \varphi_b \eta \rangle \right) +$$

$$\langle \varphi_i \varphi_j \zeta \rangle \langle \varphi_j \varphi_b \eta \rangle \langle \varphi_a \varphi_b \kappa \rangle + \langle \varphi_i \varphi_j \eta \rangle \langle \varphi_j \varphi_b \kappa \rangle \langle \varphi_a \varphi_b \zeta \rangle +$$

$$\langle \varphi_i \varphi_j \zeta \rangle \langle \varphi_j \varphi_b \kappa \rangle \langle \varphi_a \varphi_b \eta \rangle + \langle \varphi_i \varphi_j \eta \rangle \langle \varphi_j \varphi_b \zeta \rangle \langle \varphi_a \varphi_b \kappa \rangle \right) \quad (B-8)$$

$$D4 = 2 \sum_{i,j,a,b} \left( \langle \varphi_i | V_x | \varphi_a \rangle + K_{ia} \right) * F3$$

$$D5 = 2 \sum_{i,j,a,b} \left( \langle \varphi_i | V_x | \varphi_j \rangle + K_{ij} \right) * F4$$

$$F4 = \left( \langle \varphi_i \varphi_b \kappa \rangle \langle \varphi_a \varphi_b \eta \rangle \langle \varphi_j \varphi_a \zeta \rangle + \langle \varphi_i \varphi_b \zeta \rangle \langle \varphi_a \varphi_b \kappa \rangle \langle \varphi_j \varphi_a \eta \rangle \right) +$$

$$\langle \varphi_i \varphi_b \zeta \rangle \langle \varphi_a \varphi_b \eta \rangle \langle \varphi_j \varphi_a \kappa \rangle + \langle \varphi_i \varphi_b \kappa \rangle \langle \varphi_a \varphi_b \zeta \rangle \langle \varphi_j \varphi_a \eta \rangle +$$

$$\langle \varphi_i \varphi_b \zeta \rangle \langle \varphi_a \varphi_b \kappa \rangle \langle \varphi_j \varphi_a \eta \rangle + \langle \varphi_i \varphi_b \kappa \rangle \langle \varphi_a \varphi_b \zeta \rangle \langle \varphi_j \varphi_a \kappa \rangle \right) \quad (B-10)$$
\[ D6 = 2 \sum_{i,j,a,b} \frac{(< \varphi_a | V_x | \varphi_b > + K_{ab}) \ast F5}{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_a)} \]

\[ F5 = (\varphi_a \varphi_j \kappa > \varphi_i \varphi_j \eta > \varphi_i \varphi_b \zeta > + \varphi_a \varphi_j \kappa > \varphi_i \varphi_j \zeta > \varphi_i \varphi_a \eta > + \varphi_a \varphi_j \zeta > \varphi_i \varphi_j \eta > \varphi_i \varphi_b \kappa > + \varphi_a \varphi_j \eta > \varphi_i \varphi_j \kappa > \varphi_i \varphi_a \zeta > + \varphi_a \varphi_j \zeta > \varphi_i \varphi_j \kappa > \varphi_i \varphi_a \eta > + \varphi_a \varphi_j \eta > \varphi_i \varphi_j \zeta > \varphi_i \varphi_b \kappa > ) \quad (B-11) \]

\[ D7 = -2 \sum_{i,j,a,b} \frac{(< \varphi_a | V_x | \varphi_b > + K_{ab}) \ast F6}{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)(\varepsilon_j - \varepsilon_a)} \]

\[ F6 = (\varphi_i \varphi_c \kappa > \varphi_b \varphi_c \eta > \varphi_i \varphi_a \zeta > + \varphi_i \varphi_c \kappa > \varphi_b \varphi_c \zeta > \varphi_i \varphi_a \eta > + \varphi_i \varphi_c \zeta > \varphi_b \varphi_c \eta > \varphi_i \varphi_a \kappa > + \varphi_i \varphi_c \eta > \varphi_b \varphi_c \kappa > \varphi_i \varphi_a \zeta > + \varphi_i \varphi_c \zeta > \varphi_b \varphi_c \kappa > \varphi_i \varphi_a \eta > + \varphi_i \varphi_c \eta > \varphi_b \varphi_c \zeta > \varphi_i \varphi_a \kappa > ) \quad (B-12) \]

\[ D8 = -2 \sum_{i,j,k,a} \frac{(< \varphi_i | V_x | \varphi_j > + K_{ij}) \ast F2}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)(\varepsilon_k - \varepsilon_a)} \quad (B-13) \]

The second part is represented by the sum of diagrams (SX1) - (SX6)

\[ D9 = 2 \sum_{i,j,a,b} \frac{\varphi_i \varphi_a | \varphi_j \varphi_b > \ast F7}{(\varepsilon_k - \varepsilon_b)(\varepsilon_j - \varepsilon_b)(\varepsilon_i - \varepsilon_a)} \]

\[ F7 = (\varphi_b \varphi_k \kappa > \varphi_k \varphi_j \eta > \varphi_i \varphi_a \zeta > + \varphi_b \varphi_k \kappa > \varphi_k \varphi_j \zeta > \varphi_i \varphi_a \eta > + \varphi_b \varphi_k \zeta > \varphi_k \varphi_j \eta > \varphi_i \varphi_a \kappa > + \varphi_b \varphi_k \eta > \varphi_k \varphi_j \kappa > \varphi_i \varphi_a \zeta > + \varphi_b \varphi_k \zeta > \varphi_k \varphi_j \kappa > \varphi_i \varphi_a \eta > + \varphi_b \varphi_k \eta > \varphi_k \varphi_j \zeta > \varphi_i \varphi_a \kappa > ) \quad (B-14) \]

\[ D10 = -2 \sum_{i,j,a,b,c} \frac{\varphi_i \varphi_a | \varphi_j \varphi_b > \ast F8}{(\varepsilon_j - \varepsilon_c)(\varepsilon_j - \varepsilon_b)(\varepsilon_i - \varepsilon_a)} \]

\[ F8 = (\varphi_j \varphi_c \kappa > \varphi_c \varphi_b \eta > \varphi_i \varphi_a \zeta > + \varphi_j \varphi_c \kappa > \varphi_c \varphi_b \zeta > \varphi_i \varphi_a \eta > + \varphi_j \varphi_c \zeta > \varphi_c \varphi_b \eta > \varphi_i \varphi_a \kappa > + \varphi_j \varphi_c \eta > \varphi_c \varphi_b \kappa > \varphi_i \varphi_a \zeta > + \varphi_j \varphi_c \zeta > \varphi_c \varphi_b \kappa > \varphi_i \varphi_a \eta > + \varphi_j \varphi_c \eta > \varphi_c \varphi_b \zeta > \varphi_i \varphi_a \kappa > ) \quad (B-15) \]
To get final expression for $\Xi_{\eta\zeta}$ all terms D1 - D14 should be summed up.
REFERENCES


BIOGRAPHICAL SKETCH

I was born in Avdeevka, a small town located in the southeastern part of the Ukraine in the Donetsk region. I grew up in the city of Gorlovka, a working-class mining community. When I was in ninth grade, I acquired an interest in chemistry and decided that I would become a chemist. During my last year of high school, I was one of the winners of the Ukrainian Chemistry Olympiad. As a result, I was admitted to the prestigious Moscow State University without the otherwise necessary entrance examinations. During my sophomore year of college, I decided to specialize in quantum chemistry. After I defended my undergraduate thesis and obtained my degree in 2002, I began to work toward joining Dr. Rodney Bartlett’s research group at the University of Florida. After working as a system administrator for several companies in Moscow for 16 months, I obtained the necessary funds to pay for transportation to the United States as well as for the necessary exams, which included the Graduate Record Examination (GRE) and the Test of English as a Foreign Language (TOEFL). Finally, I joined Dr. Bartlett’s group at the University of Florida on January 21st, 2004.