Working equation of LR-TD-DFT
First-order polarization propagator approximation

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Abstract

We present the derivation of a new response method termed first order polarization propagator approximation. The electronic structure is given by a density functional representation. We provide a detailed derivation of the method along with explicit expressions for the relevant integrals and matrix elements.

Keywords: LR-TD-DFT, First-Order Polarization Propagater Approximation (FOPPA), Linear Response Theory, State Transfer Operators, Transition Vectors.

1 Introduction

We have presented a detailed derivation of a new response method that is denoted first-order polarization propagator approximation (FOPPA). It is a method, that bridges the time-dependent self-consistent field approach and the second-order polarization propagator (SOPPA) method.[1–3] We have formulated the method in terms of conventional response theory and give the mathematical derivation of the method. Response theory jointly with electronic structure theory has been developed within the last sixty years starting with the work by Linderberg and Ohrn.[4,5] Response

theory has clearly influenced the manner by which researchers calculate static and frequency dependent molecular properties.[6–15] The developed methods have included electronic structure methods from Hartree-Fock and density functional theory to the high-level correlated electronic structure methods such as coupled cluster and configuration interaction. Response methods have also been extended to include investigations where the investigated molecule is surrounded by an environment. The environment could be a solvent, a protein or a surface.

Generally, it is clear that theoretical and computational chemistry has pushed the boundaries for describing molecular systems, chemical reactions, and molecular properties within the last 5 decades. This has occurred due to the substantial increase of computer power along with numerous developments of new and efficient methods and numerical implementations. Therefore, theoretical and computational chemistry play an extremely important role in any modern chemical laboratory and provide crucial insight into a lot of chemical phenomena.[16] A new normal in a modern chemical laboratory is the concept of "the golden standard", namely the use of a high-level computational method. This method is the coupled cluster description of electronic structure and the specific method is termed CCSD(T).[11,17,18]

First we have introduced the underlying assumptions for the method, and we have presented the derivations using density functional theory for the electronic structure of the molecule. We continue by presenting the working equations for linear response time-dependent density functional theory and derive the FOPPA matrix equation. Based on the previous sections we are able to present explicit expressions for the matrix elements of the FOPPA matrix equations in section 4. In the final section we conclude and discuss the potential use of the method. We have given a detailed derivation of the equations that form the basis for FOPPA, and thereby we have provided a guide for new researchers to enter the world of response theory. We hope that this detailed derivation will encourage new and young researchers to engage in the further developments of response theory.

2 Linear Response TD-DFT

The extension of Kohn-Sham (KS) DFT to time-dependent DFT (TD-DFT) is obtainable due to the theorems, that validate the correspondence between the electron density and an external potential in both time-dependent and time-independent domains, deduced and proved by E. Runge and E. K. U. Gross.[19] Starting with the time-dependent Schrödinger equation.

$$i\hbar\frac{\partial}{\partial t}|\Psi^{KS}(\vec{r},t)\rangle = \hat{H}(\vec{r},t)|\Psi^{KS}(\vec{r},t)\rangle \tag{1}$$

The parameterization of the time dependence is achieved by following the framework of response theory (LR-TD-DFT).[20] The time dependence is implemented in the hamiltonian of the reference system $\hat{H}(t)$ by a perturbation. The perturbation consists of an internal field dependence of the reference system and an external field dependence.

$$\hat{H}(\vec{r},t) = \hat{H}_{ref}(\vec{r}) + \hat{H}_{ref,int}(\vec{r},t) + \hat{H}^{(1)}_{ext}(\vec{r},t) \tag{2}$$

The time-dependent KS hamiltonian for the unperturbed system is defined as:

$$\hat{H}^{KS}(\vec{r},t) = \hat{H}_{ref}(\vec{r}) + \hat{H}_{ref,int}(\vec{r},t) \tag{3}$$

The external field is turned on at t_0 by the Heaviside step function $\theta(t)$.

$$\hat{H}^{(1)}_{ext}(\vec{r},t) = \theta(t-t_0)\hat{H}^{(1)}_{ext}(\vec{r},t) \tag{4}$$

The time-dependent Schrödinger equation then becomes:

$$i\hbar\frac{\partial}{\partial t}|\Psi^{KS}(\vec{r},t)\rangle = \left(\hat{H}^{KS}(\vec{r},t) + \hat{H}^{(1)}_{ext}(\vec{r},t)\right)|\Psi^{KS}(\vec{r},t)\rangle \tag{5}$$

Since the electron density is time-dependent, the KS equation for the molecular orbitals also becomes time-dependent.

$$i\hbar\frac{\partial}{\partial t}|\varphi^{KS}_a(i,t)\rangle = \left[-\frac{1}{2}\hat{\nabla}^2_i + \hat{v}_{ext}(\vec{r_i},t) + \int\frac{\rho(\vec{r_j}',t)}{|\vec{r_i}-\vec{r_j}'|}d\vec{r_j}' + \hat{v}_{XC}(\vec{r_i},t)\right]|\varphi^{KS}_a(i,t)\rangle \tag{6}$$

$$\hat{v}_{ext}(\vec{r_i},t) = \hat{v}_{ref}(\vec{r_i}) + \hat{v}(t) \tag{7}$$

Here, i denotes the combined spatial and spin coordinate of the electron. The exchange-correlation potential is time-dependent, meaning that it depends on the

initial electron density and the entire time domain, i.e. the time-dependent KS equation has a memory. The adiabatic approximation states that the memory effects can be neglected.[21–23]

$$\hat{v}_{XC}(\vec{r_i}, t) = \hat{v}_{XC}(\vec{r_i}) \tag{8}$$

The time-dependent KS Fock operator $\hat{h}(\vec{r_i}, t)$ is defined:

$$\hat{h}(\vec{r_i}, t) = -\frac{1}{2}\hat{\nabla}_i^2 + \hat{v}_{ext}(\vec{r_i}, t) + \int \frac{\rho(\vec{r_j}', t)}{|\vec{r_i} - \vec{r_j}'|} d\vec{r_j}' + \hat{v}_{XC}(\vec{r_i}) \tag{9}$$

Hence the time-dependent KS equation can be written as:

$$i\hbar\frac{\partial}{\partial t}|\varphi_a^{KS}(i,t)\rangle = \hat{h}(\vec{r_i}, t)|\varphi_a^{KS}(i,t)\rangle \tag{10}$$

The wavefunction is time-dependent and can be expressed in terms of the unperturbed wavefunction.

$$|\Psi^{KS}(\vec{r}, t)\rangle = e^{\hat{\kappa}(t)}|\Psi^{KS,(0)}(\vec{r})\rangle \tag{11}$$

$\hat{\kappa}(t)$ is the anti-hermitian time propagation operator, and it is defined in terms of operators from second quantization theory for convenience. The operator that takes one electron form φ_i and place it in φ_a is defined as:

$$\hat{q_2} = \langle\varphi_a|\hat{q_1}|\varphi_i\rangle\hat{E}_{ai} = \sum_{ai} A_{ai} \sum_{\sigma} \hat{a}_{a\sigma}^{\dagger}\hat{a}_{i\sigma} \tag{12}$$

$A_{ai} = \langle\varphi_a|\hat{q_1}|\varphi_i\rangle$ is the matrix element, and $\hat{E}_{ia} = \hat{a}_{a\sigma}^{\dagger}\hat{a}_{i\sigma}$ is the excitation operator consisting of $\hat{a}_{a\sigma}^{\dagger}$ and $\hat{a}_{i\sigma}$, which are the creation and annihilation operators with respect to one electron in an orbital with spin σ, respectively. $\hat{q_1}$ is an operator that first annihilate and then create an electron in the same orbital.

Hence $\hat{\kappa}(t)$ is defined as:

$$\hat{\kappa}(t) = \sum_{ai} \kappa_{ai}(t)\hat{E}_{ai} \qquad \hat{\kappa}(t)^{\dagger} = -\hat{\kappa}(t) \tag{13}$$

The electron density is similarly described in terms of second quantization theory.

$$\hat{\rho}(\vec{r}) = \langle\varphi_a^{KS}(\vec{r}')|\sum_{ai}\delta(\vec{r}' - \vec{r})|\varphi_i^{KS}(\vec{r}')\rangle\hat{E}_{ai} = \sum_{ai}\varphi_a^{KS}(\vec{r})^*\varphi_i^{KS}(\vec{r})\hat{E}_{ai} \tag{14}$$

The time dependence of the electron density is caused by the time-dependent wavefunction.

$$\rho(\vec{r},t) = \langle \Psi^{KS}(\vec{r},t)|\hat{\rho}(\vec{r})|\Psi^{KS}(\vec{r},t)\rangle \tag{15}$$
$$= \langle \Psi^{KS,(0)}(\vec{r})|e^{\hat{\kappa}(t)}\hat{\rho}(\vec{r})e^{-\hat{\kappa}(t)}|\Psi^{KS,(0)}(\vec{r})\rangle \tag{16}$$

The electron density and the time propagation operator can be expanded in terms of perturbation order.

$$\rho(\vec{r},t) = \rho^{(0)}(\vec{r}) + \rho^{(1)}(\vec{r},t) + \rho^{(2)}(\vec{r},t) + ... \tag{17}$$
$$\hat{\kappa}(t) = 0 + \hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + ... \tag{18}$$

The Taylor series expansion of the exponential time propagation operator is:

$$e^{\hat{\kappa}(t)} = 1 + (\hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + ...) + \frac{1}{2}(\hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + ...)^2 + ... \tag{19}$$

If a weak field is considered, only the zeroth order and the linear term contribute to the expansion.[20] Writing out the electron density and collecting terms up to first order gives:

$$\rho(\vec{r},t) = \langle \Psi^{KS,(0)}(\vec{r})|e^{\hat{\kappa}(t)}\hat{\rho}(\vec{r})e^{-\hat{\kappa}(t)}|\Psi^{KS,(0)}(\vec{r})\rangle \tag{20}$$
$$= \langle \Psi^{KS,(0)}(\vec{r})|\hat{\rho}^{(0)}(\vec{r})|\Psi^{KS,(0)}(\vec{r})\rangle \tag{21}$$
$$+ \langle \Psi^{KS,(0)}(\vec{r})|[\hat{\kappa}^{(1)}(t), \hat{\rho}^{(0)}(\vec{r})]|\Psi^{KS,(0)}(\vec{r})\rangle + ... \tag{22}$$

The unperturbed and first order perturbed electron densities are identified.

$$\rho^{(0)}(\vec{r}) = \langle \Psi^{KS,(0)}(\vec{r})|\hat{\rho}^{(0)}(\vec{r})|\Psi^{KS,(0)}(\vec{r})\rangle \tag{23}$$
$$= \sum_{ai} \varphi_a^{KS}(\vec{r})^* \varphi_i^{KS}(\vec{r}) \langle \Psi^{KS,(0)}(\vec{r})|\hat{E}_{ai}|\Psi^{KS,(0)}(\vec{r})\rangle \tag{24}$$

$$\rho^{(1)}(\vec{r},t) = \langle \Psi^{KS,(0)}(\vec{r})|[\hat{\kappa}^{(1)}(t), \hat{\rho}^{(0)}(\vec{r})]|\Psi^{KS,(0)}(\vec{r})\rangle \tag{25}$$
$$= \sum_{ai} \varphi_a^{KS}(\vec{r})^* \varphi_i^{KS}(\vec{r}) \langle \Psi^{KS,(0)}(\vec{r})|[\hat{\kappa}^{(1)}(t), \hat{E}_{ai}]|\Psi^{KS,(0)}(\vec{r})\rangle \tag{26}$$

Defining the perturbation density matrices $D_{ai}^{(n)}$.

$$D_{ai}^{(0)} = \langle \Psi^{KS,(0)}(\vec{r})|\hat{E}_{ai}|\Psi^{KS,(0)}(\vec{r})\rangle \tag{27}$$

$$D_{ai}^{(1)}(t) = \langle \Psi^{KS,(0)}(\vec{r})|[\hat{\kappa}^{(1)}(t), \hat{E}_{ai}]|\Psi^{KS,(0)}(\vec{r})\rangle \tag{28}$$

Hence, the unperturbed and first order perturbed electron densities can be written as:

$$\rho^{(0)}(\vec{r}) = \sum_{ai} \varphi_a^{KS}(\vec{r})^* \varphi_i^{KS}(\vec{r}) D_{ai}^{(0)} \tag{29}$$

$$\rho^{(1)}(\vec{r},t) = \sum_{ai} \varphi_a^{KS}(\vec{r})^* \varphi_i^{KS}(\vec{r}) D_{ai}^{(1)}(t) \tag{30}$$

The hamiltonian of the system is already expanded in orders of perturbation. In general:

$$\hat{H}(\vec{r},t) = \sum_{n=1} \hat{H}^{KS,(n)}(\vec{r},t) = \sum_{n=1} \sum_{ai} \hat{h}_{ai}^{KS,(n)}(\vec{r_i},t)\hat{E}_{ai} \tag{31}$$

$$\begin{aligned}
\hat{h}_{ai}^{KS,(n)}(\vec{r_i},t) &= \langle \varphi_a^{KS}(\vec{r})|\delta\hat{h}_i^{KS} + \hat{j}^{(n)}(t) + \hat{v}_{XC}^{(n)}(t)|\varphi_i^{KS}(\vec{r})\rangle && (32)\\
&= \langle \varphi_a^{KS}(\vec{r})|\delta\hat{h}_i^{KS}|\varphi_i^{KS}(\vec{r})\rangle + \langle \varphi_a^{KS}(\vec{r})|\hat{j}^{(n)}(t)|\varphi_i^{KS}(\vec{r})\rangle && (33)\\
&\quad + \langle \varphi_a^{KS}(\vec{r})|\hat{v}_{XC}^{(n)}(t)|\varphi_i^{KS}(\vec{r})\rangle && (34)\\
&= \delta\hat{h}_{ai}^{KS} + \hat{j}_{ai}^{(n)}(t) + \hat{v}_{XC,ai}^{(n)}(t) && (35)
\end{aligned}$$

$\hat{h}_{ai}^{KS}$ does not contribute to any perturbations, since it does not depend on the electron density. Similar to the electron density and the time propagation operator, only terms up to the first order perturbation is considered. The matrix elements are evaluated.

$$\begin{aligned}
\hat{j}_{ai}^{(1)}(t) &= \langle \varphi_a^{KS}(\vec{r})|\hat{j}^{(1)}(t)|\varphi_i^{KS}(\vec{r})\rangle && (36)\\
&= \langle \varphi_a^{KS}(\vec{r})| \int \frac{\rho^{(1)}(\vec{r'},t)}{|\vec{r'}-\vec{r}|} d\vec{r'} |\varphi_i^{KS}(\vec{r})\rangle && (37)\\
&= \sum_{bj} \langle \varphi_a^{KS}(\vec{r})\varphi_b^{KS}(\vec{r'})| \frac{1}{|\vec{r'}-\vec{r}|} |\varphi_i^{KS}(\vec{r})\varphi_j^{KS}(\vec{r'})\rangle D_{ai}^{(1)}(t) && (38)\\
&= \sum_{bj} g_{aibj} D_{ai}^{(1)}(t), \quad g_{aibj} = \langle \varphi_a^{KS}(\vec{r})\varphi_b^{KS}(\vec{r'})| \frac{1}{|\vec{r'}-\vec{r}|} |\varphi_i^{KS}(\vec{r})\varphi_j^{KS}(\vec{r'})\rangle && (39)
\end{aligned}$$

$$\begin{aligned}
\hat{v}_{XC,ai}^{(1)}(t) &= \langle \varphi_a^{KS}(\vec{r})|\hat{v}_{XC}^{(1)}(t)|\varphi_i^{KS}(\vec{r})\rangle && (40)\\
&= \langle \varphi_a^{KS}(\vec{r})| \int \frac{\delta\hat{v}_{XC}}{\delta\rho(\vec{r})} \rho^{(1)}(\vec{r'},t) d\vec{r'} |\varphi_i^{KS}(\vec{r})\rangle && (41)
\end{aligned}$$

The expectation values of time-independent operators $\hat{P}$ can be evaluated. The first order perturbation of the expectation value becomes:

$$\begin{aligned}
\langle \Psi^{KS}(\vec{r},t)|\hat{P}|\Psi^{KS}(\vec{r},t)\rangle^{(1)} &= \langle \Psi^{KS,(0)}(\vec{r})|e^{\hat{\kappa}(t)}\hat{P}e^{-\hat{\kappa}(t)}|\Psi^{KS,(0)}(\vec{r})\rangle && (42)\\
&= \langle \Psi^{KS,(0)}(\vec{r})|[\hat{\kappa}^{(1)}(t),\hat{P}]|\Psi^{KS,(0)}(\vec{r})\rangle && (43)
\end{aligned}$$

However, it is more convenient to write $\hat{\kappa}^{(1)}(t)$ in terms of frequency, since frequency dependent properties are desirable and easier to handle. The domain-transformation

is achieved by the Fourier transform.

$$\hat{\kappa}^{(1)}(t) = \int_{-\infty}^{\infty} \hat{\kappa}_{\omega}^{(1)} e^{-i\omega t} d\omega \tag{44}$$

The expectation value of the time-independent operator can then be written as:

$$\langle \Psi^{KS,(0)}(\vec{r})|[\hat{\kappa}^{(1)}(t), \hat{P}]|\Psi^{KS,(0)}(\vec{r})\rangle = \int_{-\infty}^{\infty} e^{-i\omega t} \langle \Psi^{KS,(0)}(\vec{r})|[\kappa_{\omega}^{(1)}, \hat{P}]|\Psi^{KS,(0)}(\vec{r})\rangle d\omega \tag{45}$$

The linear response of the expectation value is:[3]

$$\langle \Phi(t, \vec{F}(t))|\hat{P}|\Phi(t, \vec{F}(t))\rangle^{(1)} = \sum_{\alpha} \int_{-\infty}^{\infty} F_{\alpha}(\tau) \frac{-i}{\hbar} \theta(t-\tau) \langle \Phi_0^{(0)}|[\hat{P}_I(t), \hat{O}_{\alpha,I}(\tau)]|\Phi_0^{(0)}\rangle d\tau \tag{46}$$

$\hat{O}_{\alpha,I}(\tau)$ is a perturbation operator, $\hat{P}_I(t)$ the interacting representation of $\hat{P}$, and $F_{\alpha}(\tau)$ is the field strength. Identifying the hamiltonian for the linear response and defining the linear response function $\langle\langle \hat{P}_I(t); \hat{O}_{\alpha,I}(\tau)\rangle\rangle$.

$$\hat{H}^{(1)}(t) = \sum_{\alpha} F_{\alpha}(\tau) \hat{O}_{\alpha,I}(\tau) \tag{47}$$

$$\langle\langle \hat{P}_I(t); \hat{O}_{\alpha,I}(\tau)\rangle\rangle = \frac{-i}{\hbar} \theta(t-\tau) \langle \Phi_0^{(0)}|[\hat{P}_I(t), \hat{O}_{\alpha,I}(\tau)]|\Phi_0^{(0)}\rangle \tag{48}$$

Hence, the expectation value for the linear response can be written as:

$$\langle \Phi(t, \vec{F}(t))|\hat{P}|\Phi(t, \vec{F}(t))\rangle^{(1)} = \int_{-\infty}^{\infty} \langle\langle \hat{P}_I(t); \hat{H}^{(1)}(t)\rangle\rangle d\tau \tag{49}$$

The transformation from time domain to frequency domain, for the first order perturbed hamiltonian, is similarly done by the Fourier transformation.

$$\hat{H}^{(1)}(t) = \int_{-\infty}^{\infty} \hat{H}_{\omega}^{(1)} e^{-i\omega t} d\omega \tag{50}$$

The linear response of the expectation value becomes:

$$\langle \Phi(t, \vec{F}(t))|\hat{P}|\Phi(t, \vec{F}(t))\rangle^{(1)} = \int_{-\infty}^{\infty} e^{-i\omega t} \langle\langle \hat{P}_I(t); \hat{H}_{\omega}^{(1)}\rangle\rangle_{\omega} d\omega \tag{51}$$

Thus, the linear response function can then be identified as:

$$\langle\langle \hat{P}_I(t); \hat{H}_{\omega}^{(1)}\rangle\rangle_{\omega} = \langle \Psi^{KS,(0)}(\vec{r})|[\hat{\kappa}_{\omega}^{(1)}, \hat{P}]|\Psi^{KS,(0)}(\vec{r})\rangle \tag{52}$$

$\hat{\kappa}_\omega^{(1)}$ still needs to be parameterized, and in order to do so, a new time-independent operator $\hat{Q}$ is considered. The operator $\hat{Q}$ is made time-dependent by an unitary transformation.

$$\hat{Q}(t) = e^{-\hat{\kappa}(t)}\hat{Q}e^{\hat{\kappa}(t)} \tag{53}$$

The expectation value of $\hat{Q}(t)$ is:

$$\langle\Psi^{KS}(\vec{r},t)|\hat{Q}(t)|\Psi^{KS}(\vec{r},t)\rangle = \langle\Psi^{KS,(0)}(\vec{r})|e^{\hat{\kappa}(t)}e^{-\hat{\kappa}(t)}\hat{Q}e^{\hat{\kappa}(t)}e^{-\hat{\kappa}(t)}|\Psi^{KS,(0)}(\vec{r})\rangle \tag{54}$$

$$= \langle\Psi^{KS,(0)}(\vec{r})|\hat{Q}|\Psi^{KS,(0)}(\vec{r})\rangle \tag{55}$$

Taking the derivative with respect to time on both sides of the previous equation results in a zero on the right hand side, since neither depend on the time.

$$(\frac{\partial}{\partial t}\langle\Psi^{KS}(\vec{r},t)|)\hat{Q}(t)|\Psi^{KS}(\vec{r},t)\rangle + \langle\Psi^{KS}(\vec{r},t)|\frac{\partial\hat{Q}(t)}{\partial t}|\Psi^{KS}(\vec{r},t)\rangle + \langle\Psi^{KS}(\vec{r},t)|\hat{Q}(t)\frac{\partial}{\partial t}|\Psi^{KS}(\vec{r},t)\rangle = 0 \tag{56}$$

The derivative of the wavefunction is given by the time-dependent Schrödinger equation.

$$\frac{\partial}{\partial t}|\Psi^{KS}(\vec{r},t)\rangle = \frac{1}{i\hbar}(\hat{H}^{KS}(\vec{r},t) + \hat{H}_{ext}^{(1)}(\vec{r},t))|\Psi^{KS}(\vec{r},t)\rangle \tag{57}$$

Thus, substituting the expression into the eqn. (56), the Ehrenfest theorem is obtained. The Ehrenfest theorem describes how the expectation value evolves in time.

$$-\frac{1}{i\hbar}(\hat{H}^{KS}(\vec{r},t) + \hat{H}_{ext}^{(1)}(\vec{r},t))\hat{Q}(t)|\Psi^{KS}(\vec{r},t)\rangle + \langle\Psi^{KS}(\vec{r},t)|\frac{\partial\hat{Q}(t)}{\partial t}|\Psi^{KS}(\vec{r},t)\rangle + \frac{1}{i\hbar}\hat{Q}(t)(\hat{H}^{KS}(\vec{r},t) + \hat{H}_{ext}^{(1)}(\vec{r},t))|\Psi^{KS}(\vec{r},t)\rangle = 0 \tag{58}$$

$$\Leftrightarrow \langle\Psi^{KS}(\vec{r},t)|i\hbar\frac{\partial\hat{Q}(t)}{\partial t} + [\hat{Q}(t), \hat{H}^{KS}(\vec{r},t) + \hat{H}_{ext}^{(1)}(\vec{r},t)]|\Psi^{KS}(\vec{r},t)\rangle = 0 \tag{59}$$

In order to collect all terms in one commutator, the first term is rewritten.

$$\langle\Psi^{KS}(\vec{r},t)|i\hbar\frac{\partial\hat{Q}(t)}{\partial t}|\Psi^{KS}(\vec{r},t)\rangle = i\hbar\langle\Psi^{KS}(\vec{r},t)|\frac{\partial e^{-\hat{\kappa}(t)}\hat{Q}e^{\hat{\kappa}(t)}}{\partial t}|\Psi^{KS}(\vec{r},t)\rangle \tag{60}$$

$$= i\hbar\langle\Psi^{KS}(\vec{r},t)|[\hat{Q}(t), \frac{\partial\hat{\kappa}(t)}{\partial t}]|\Psi^{KS}(\vec{r},t)\rangle \tag{61}$$

Hence, the Ehrenfest theorem can be written as:

$$\langle\Psi^{KS}(\vec{r},t)|[\hat{Q}(t), \hat{H}^{KS}(\vec{r},t) + \hat{H}_{ext}^{(1)}(\vec{r},t) + i\hbar\frac{\partial\hat{\kappa}(t)}{\partial t}]|\Psi^{KS}(\vec{r},t)\rangle = 0 \tag{62}$$

This equation can be expanded in orders of perturbations. Including only the unperturbed and first order perturbation the equation becomes:

$$\langle\Psi^{KS,(0)}(\vec{r})|[\hat{Q},\hat{H}^{(1)}_{ext}(\vec{r},t)+i\hbar\frac{\partial\hat{\kappa}^{(1)}(t)}{\partial t}]|\Psi^{KS,(0)}(\vec{r})\rangle + \langle\Psi^{KS,(0)}(\vec{r})|\left\{e^{\hat{\kappa}(t)}[e^{-\hat{\kappa}(t)}\hat{Q}e^{\hat{\kappa}(t)},\hat{H}^{KS}(\vec{r},t)]e^{-\hat{\kappa}(t)}\right\}|\Psi^{KS,(0)}(\vec{r})\rangle^{(1)}=0 \quad (63)$$

The last term is the first order correction and is denoted $\langle\rangle^{(1)}$. It can be rewritten by expanding the exponential time propagation operator and neglecting higher order terms.

$$\langle\rangle^{(1)} = \langle\Psi^{KS,(0)}(\vec{r})|\left\{e^{\hat{\kappa}(t)}[e^{-\hat{\kappa}(t)}\hat{Q}e^{\hat{\kappa}(t)},\hat{H}^{KS}(\vec{r},t)]e^{-\hat{\kappa}(t)}\right\}|\Psi^{KS,(0)}(\vec{r})\rangle^{(1)} \quad (64)$$

$$= \langle\Psi^{KS,(0)}(\vec{r})|\Big\{\hat{Q}(1+\hat{\kappa}^{(1)}(t))\hat{H}^{KS}(\vec{r},t)(1-\hat{\kappa}^{(1)}(t)) \quad (65)$$

$$-(1+\hat{\kappa}^{(1)}(t))\hat{H}^{KS}(\vec{r},t)(1-\hat{\kappa}^{(1)}(t))\hat{Q}\Big\}|\Psi^{KS,(0)}(\vec{r})\rangle^{(1)} \quad (66)$$

$$= \langle\Psi^{KS,(0)}(\vec{r})|[\hat{Q},[\hat{\kappa}^{(1)}(t)),\hat{H}^{KS,(0)}(\vec{r},t)]+\hat{H}^{KS,(1)}(\vec{r},t)]|\Psi^{KS,(0)}(\vec{r})\rangle \quad (67)$$

Substituting $\langle\rangle^{(1)}$ into the eqn. (63) and moving $\langle\Psi^{KS,(0)}(\vec{r})|[\hat{Q},\hat{H}^{(1)}_{ext}(\vec{r},t)]|\Psi^{KS,(0)}(\vec{r})\rangle$ over to the other side by using the commutator property $[a,b]=-[b,a]$.

$$\langle\Psi^{KS,(0)}(\vec{r})|[\hat{Q},[\hat{\kappa}^{(1)}(t)),\hat{H}^{KS,(0)}(\vec{r},t)]+\hat{H}^{KS,(1)}(\vec{r},t)+i\hbar\frac{\partial\hat{\kappa}^{(1)}(t)}{\partial t}]|\Psi^{KS,(0)}(\vec{r})\rangle = \langle\Psi^{KS,(0)}(\vec{r})|[\hat{H}^{(1)}_{ext}(\vec{r},t),\hat{Q}]|\Psi^{KS,(0)}(\vec{r})\rangle \quad (68)$$

Writing $\hat{\kappa}^{(1)}(t)$ and $\hat{H}^{(1)}(t)$ in their Fourier transformations and rearranging the equation.

$$\int_{-\infty}^{\infty} e^{-i\omega t}\langle\Psi^{KS,(0)}(\vec{r})|[\hat{Q},[\hat{\kappa}^{(1)}_{\omega},\hat{H}^{KS,(0)}(\vec{r},t)]+\hat{H}^{KS,(1)}_{\omega} + \hbar\omega\hat{\kappa}^{(1)}_{\omega}]|\Psi^{KS,(0)}(\vec{r})\rangle d\omega = \int_{-\infty}^{\infty} e^{-i\omega t}\langle\Psi^{KS,(0)}(\vec{r})|[\hat{H}^{(1)}_{\omega,ext},\hat{Q}]|\Psi^{KS,(0)}(\vec{r})\rangle d\omega \quad (69)$$

Since Fourier transformations are uniquely determined, the following can be concluded.

$$\langle\Psi^{KS,(0)}(\vec{r})|[\hat{Q},[\hat{\kappa}^{(1)}_{\omega},\hat{H}^{KS,(0)}(\vec{r},t)]+\hat{H}^{KS,(1)}_{\omega}+\hbar\omega\hat{\kappa}^{(1)}_{\omega}]|\Psi^{KS,(0)}(\vec{r})\rangle = \langle\Psi^{KS,(0)}(\vec{r})|[\hat{H}^{(1)}_{\omega,ext},\hat{Q}]|\Psi^{KS,(0)}(\vec{r})\rangle \quad (70)$$

In principal, this is the fundamental equation of LR-TD-DFT, however, for the purpose of numerical implementation, it is desirable to rewrite it as a system of equations. Starting with $\hat{\kappa}_{\omega}^{(1)}$ and writing:

$$\hat{\kappa}_{\omega}^{(1)} = \sum_{ai} \kappa_{\omega,ai}^{(1)} \hat{E}_{ai} = \mathbf{q}^{\dagger} \boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})} \tag{71}$$

$\mathbf{q}^{\dagger}$ and $\boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})}$ are defined as:

$$\mathbf{q}^{\dagger} = \begin{pmatrix} \cdots \hat{E}_{ai} \cdots \end{pmatrix} \qquad \boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})} = \begin{pmatrix} \vdots \\ \kappa_{\omega,ai}^{(1)} \\ \vdots \end{pmatrix} \tag{72}$$

The time-independent operator $\hat{Q}$ can then be expressed as a linear combination of the elements in $\mathbf{q}$, resulting in a set of equations.

$$\begin{aligned} \langle \Psi^{KS,(0)}(\vec{r}) | [\hat{\mathbf{q}}, [\hat{\kappa}_{\omega}^{(1)}, \hat{H}^{KS,(0)}(\vec{r},t)] + \hat{H}_{\omega}^{KS,(1)} + \hbar\omega \hat{\kappa}_{\omega}^{(1)}] | \Psi^{KS,(0)}(\vec{r}) \rangle \\ = \langle \Psi^{KS,(0)}(\vec{r}) | [\hat{H}_{\omega,ext}^{(1)}, \hat{\mathbf{q}}] | \Psi^{KS,(0)}(\vec{r}) \rangle \end{aligned} \tag{73}$$

Similar, writing $\hat{H}_{\omega,ext}^{(1)}$ as:

$$\hat{H}_{\omega,ext}^{(1)} = \sum_{ai} \hat{h}_{\omega,ai}^{KS,(1)} \hat{E}_{ai} \tag{74}$$

$$\hat{h}_{\omega,ai}^{KS,(1)} = \hat{j}_{\omega,ai}^{(1)} + \hat{v}_{XC,\omega,ai}^{(1)} \tag{75}$$

The operators in $\hat{h}^{KS,(1)}$ can be rewritten.

$$\hat{j}_{\omega,ai}^{(1)} + \hat{v}_{XC,\omega,ai}^{(1)} = \sum_{bj} g_{aibj} D_{\omega,ai}^{(1)} + \langle \varphi_a^{KS}(\vec{r}) | \int \frac{\delta \hat{v}_{XC}}{\delta \rho(\vec{r})} \rho^{(1)}(\vec{r}', t) d\vec{r} | \varphi_i^{KS}(\vec{r}) \rangle \tag{76}$$

$$= \sum_{bj} \langle \varphi_a^{KS}(\vec{r}) \varphi_b^{KS}(\vec{r}') | \frac{1}{|\vec{r}' - \vec{r}|} | \varphi_i^{KS}(\vec{r}) \varphi_j^{KS}(\vec{r}') \rangle \tag{77}$$

$$\times \langle \Psi^{KS,(0)}(\vec{r}) | [\hat{\kappa}_{\omega}^{(1)}, \hat{E}_{bj}] | \Psi^{KS,(0)}(\vec{r}) \rangle \tag{78}$$

$$+ \sum_{bj} \langle \varphi_a^{KS}(\vec{r}) | \int \frac{\delta \hat{v}_{XC}}{\delta \rho(\vec{r})} \varphi_b^{KS}(\vec{r}')^* \varphi_j^{KS}(\vec{r}') d\vec{r}' | \varphi_i^{KS}(\vec{r}) \rangle \tag{79}$$

$$\times \langle \Psi^{KS,(0)}(\vec{r}) | [\hat{\kappa}_{\omega}^{(1)}, \hat{E}_{bj}] | \Psi^{KS,(0)}(\vec{r}) \rangle \tag{80}$$

$$= \sum_{bj} \left[\frac{1}{|\vec{r}' - \vec{r}|} + \frac{\delta \hat{v}_{XC}}{\delta \rho(\vec{r})} \right]_{aibj} \langle \Psi^{KS,(0)}(\vec{r}) | [\hat{\kappa}_{\omega}^{(1)}, \hat{E}_{bj}] | \Psi^{KS,(0)}(\vec{r}) \rangle \tag{81}$$

$$\left[\frac{1}{|\vec{r}' - \vec{r}|} + \frac{\delta \hat{v}_{XC}}{\delta \rho(\vec{r})}\right]_{aibj} = \langle \varphi_a^{KS}(\vec{r}) \varphi_b^{KS}(\vec{r}')| \frac{1}{|\vec{r}' - \vec{r}|} + \frac{\delta \hat{v}_{XC}}{\delta \rho(\vec{r})} |\varphi_i^{KS}(\vec{r}) \varphi_j^{KS}(\vec{r}')\rangle \tag{82}$$

Substituting $\hat{h}_{\omega,ai}^{KS,(1)}$ and $\hat{\kappa}_{\omega}^{(1)}$ into eqn. (73) and rearranging gives:

$$\begin{aligned}
&\langle \Psi^{KS,(0)}(\vec{r})| \Big[\hat{\mathbf{q}}, [\mathbf{q}^\dagger, \hat{H}^{KS,(0)}(\vec{r}, t)]\Big] |\Psi^{KS,(0)}(\vec{r})\rangle \boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})} + \sum_{aibj} \langle \Psi^{KS,(0)}(\vec{r})| [\hat{\mathbf{q}}, \hat{E}_{ai}] \\
&\quad \times |\Psi^{KS,(0)}(\vec{r})\rangle \left[\frac{1}{|\vec{r}' - \vec{r}|} + \frac{\delta \hat{v}_{XC}}{\delta \rho(\vec{r})}\right]_{aibj} \langle \Psi^{KS,(0)}(\vec{r})| [\mathbf{q}^\dagger, \hat{E}_{bj}] |\Psi^{KS,(0)}(\vec{r})\rangle \boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})} \\
&+ \hbar\omega \langle \Psi^{KS,(0)}(\vec{r})| [\hat{\mathbf{q}}, \mathbf{q}^\dagger] |\Psi^{KS,(0)}(\vec{r})\rangle \boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})} = \langle \Psi^{KS,(0)}(\vec{r})| [\hat{H}_{\omega,ext}^{(1)}, \hat{\mathbf{q}}] |\Psi^{KS,(0)}(\vec{r})\rangle
\end{aligned} \tag{83}$$

The electronic Hessian matrix $\mathbf{E}$, the overlap matrix $\mathbf{S}$ and the first order Hamiltonian matrix $\hat{\mathbf{H}}_{\omega,\mathbf{ext}}^{(\mathbf{1})}$ are defined.

$$\begin{aligned}
\mathbf{E} = &\langle \Psi^{KS,(0)}(\vec{r})| \Big[\hat{\mathbf{q}}, [\mathbf{q}^\dagger, \hat{H}^{KS,(0)}(\vec{r}, t)]\Big] |\Psi^{KS,(0)}(\vec{r})\rangle + \sum_{aibj} \langle \Psi^{KS,(0)}(\vec{r})| [\hat{\mathbf{q}}, \hat{E}_{ai}] \\
&\times |\Psi^{KS,(0)}(\vec{r})\rangle \left[\frac{1}{|\vec{r}' - \vec{r}|} + \frac{\delta \hat{v}_{XC}}{\delta \rho(\vec{r})}\right]_{aibj} \langle \Psi^{KS,(0)}(\vec{r})| [\mathbf{q}^\dagger, \hat{E}_{bj}] |\Psi^{KS,(0)}(\vec{r})\rangle
\end{aligned} \tag{84}$$

$$\mathbf{S} = \langle \Psi^{KS,(0)}(\vec{r})| [\mathbf{q}^\dagger, \hat{\mathbf{q}}] |\Psi^{KS,(0)}(\vec{r})\rangle \tag{85}$$

$$\mathbf{H}_{\boldsymbol{\omega},\mathbf{ext}}^{(\mathbf{1})} = \langle \Psi^{KS,(0)}(\vec{r})| [\hat{H}_{\omega,ext}^{(1)}, \hat{\mathbf{q}}] |\Psi^{KS,(0)}(\vec{r})\rangle \tag{86}$$

The expression for $\boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})}$ can finally be established.

$$(\mathbf{E} - \hbar\omega\mathbf{S}) \boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})} = \mathbf{H}_{\boldsymbol{\omega},\mathbf{ext}}^{(\mathbf{1})} \tag{87}$$

$$\Leftrightarrow \boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})} = (\mathbf{E} - \hbar\omega\mathbf{S})^{-1} \mathbf{H}_{\boldsymbol{\omega},\mathbf{ext}}^{(\mathbf{1})} \tag{88}$$

With the parameterization of $\boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})}$ the linear response function can be rewritten as:[24]

$$\langle\langle \hat{P}_I(t); \hat{H}_{\omega}^{(1)} \rangle\rangle_{\omega} = \langle \Psi^{KS,(0)}(\vec{r})| [\hat{\kappa}_{\omega}^{(1)}, \hat{P}] |\Psi^{KS,(0)}(\vec{r})\rangle \tag{89}$$

$$= \langle \Psi^{KS,(0)}(\vec{r})| [\mathbf{q}^\dagger, \hat{P}] |\Psi^{KS,(0)}(\vec{r})\rangle \boldsymbol{\kappa}_{\boldsymbol{\omega}}^{(\mathbf{1})} \tag{90}$$

$$= \mathbf{P}^\dagger (\mathbf{E} - \hbar\omega\mathbf{S})^{-1} \mathbf{H}_{\boldsymbol{\omega},\mathbf{ext}}^{(\mathbf{1})} \tag{91}$$

$\mathbf{P}$ being the matrix element:

$$\mathbf{P} = \langle \Psi^{KS,(0)}(\vec{r}) | [\mathbf{q}, \hat{P}] | \Psi^{KS,(0)}(\vec{r}) \rangle \tag{92}$$

The excitation energies are calculated as poles of the linear response function, and the transition dipole moments as residuals by the electronic dipole moment operator $\hat{\vec{\mu}}$. Localizing the poles is equivalent to solving the matrix problem.

$$\mathbf{E} = \hbar\omega\mathbf{S} \tag{93}$$

3 Working equation of LR-TD-DFT

The application of response theory to TD-DFT resulted in the following linear response function:[24]

$$\langle\langle \hat{P}_I(t); \hat{H}^{(1)}_{\omega} \rangle\rangle_{\omega} = \mathbf{P}^{\dagger}(\mathbf{E} - \hbar\omega\mathbf{S})^{-1}\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}} \tag{94}$$

The vertical excitation energy from the ground state $|\Psi^{(0)}_0\rangle$ to the I-th excited state $|\Psi^{(0)}_I\rangle$ is evaluated as a pole of the linear response function. The linear response function has a pole if and only if $\mathbf{E} = \hbar\omega\mathbf{S}$, which can be formulated as the following pole condition.

$$\hbar\omega\mathbf{S} - \mathbf{E} = 0 \tag{95}$$

The principal propagator matrix $\mathbf{M}$ is defined as:

$$\mathbf{M} = \hbar\omega\mathbf{S} - \mathbf{E} \tag{96}$$

The principal propagator matrix is singular, when the frequency is:

$$\omega = \pm\frac{E^{(0)}_I - E^{(0)}_0}{\hbar}, \qquad \mathbf{S} = 1 \tag{97}$$

Now, one can search directly for the poles of the linear response function.[3] However, if the principal propagator matrix is singular, then there exists a non-trivial solution for the linear equation:

$$(\hbar\omega\mathbf{S} - \mathbf{E})\mathbf{X} = 0 \tag{98}$$

$\mathbf{X}$ being a vector containing the corresponding eigenstates. Rearranging the equation and forming the following eigenvalue problem:

$$\mathbf{EX} = \hbar\omega\mathbf{SX} \tag{99}$$

All excited states must be generated from a reference state and a complete basis set consisting of all excitation and de-excitation operators $\{{}^{\mathbf{e}}\hat{\mathbf{h}}_{\mathbf{0}}, {}^{\mathbf{d}}\hat{\mathbf{h}}_{\mathbf{0}}, {}^{\mathbf{e}}\hat{\mathbf{h}}_{\mathbf{1}}, {}^{\mathbf{d}}\hat{\mathbf{h}}_{\mathbf{1}}, ...{}^{\mathbf{e}}\hat{\mathbf{h}}_{\mathbf{n}}, {}^{\mathbf{d}}\hat{\mathbf{h}}_{\mathbf{n}}\}$. The superscripts e and d stand for excitation and de-excitation respectively, and n is the number of electrons involved. The KS ground state is the reference state for TD-DFT. Thus all excited states can be generated by:

$$|\Psi_I^{(0)}\rangle = \hat{\mathbf{h}}_{\mathbf{n}}|\Psi_0^{(0)}\rangle \tag{100}$$

The operators are called state transfer operators, and the time-dependent operators $\mathbf{q}$ from the expression of the electronic Hessian matrix $\mathbf{E}$, the overlap matrix $\mathbf{S}$, perturbation matrix $\mathbf{P}$ and the first order Hamiltonian matrix $\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}$ are expressed in terms of the state transfer operators. The following notation is used.[3]

$$\hat{\mathbf{h}}_{\mathbf{1}} = \begin{pmatrix} {}^{\mathbf{e}}\hat{\mathbf{h}}_{\mathbf{1}} \\ {}^{\mathbf{d}}\hat{\mathbf{h}}_{\mathbf{1}} \end{pmatrix} = \begin{pmatrix} \hat{\mathbf{q}}^{\dagger} \\ \hat{\mathbf{q}} \end{pmatrix} \tag{101}$$

$$\hat{\mathbf{h}}_{\mathbf{2}} = \begin{pmatrix} {}^{\mathbf{e}}\hat{\mathbf{h}}_{\mathbf{2}} \\ {}^{\mathbf{d}}\hat{\mathbf{h}}_{\mathbf{2}} \end{pmatrix} = \begin{pmatrix} \hat{\mathbf{q}}^{\dagger}\hat{\mathbf{q}}^{\dagger} \\ \hat{\mathbf{q}}\hat{\mathbf{q}} \end{pmatrix} \tag{102}$$

$$\vdots \tag{103}$$

With a complete set of state transfer operators, the linear response function can be written as:

$$\langle\langle \hat{P}_I(t); \hat{H}^{(1)}_{\omega}\rangle\rangle_{\omega} = \begin{pmatrix} \mathbf{T}^{\mathbf{T}}_{\mathbf{1}}(\mathbf{P}^{\dagger}) & \mathbf{T}^{\mathbf{T}}_{\mathbf{2}}(\mathbf{P}^{\dagger}) & \cdots \end{pmatrix} \begin{pmatrix} \mathbf{M_{11}} & \mathbf{M_{12}} & \cdots \\ \mathbf{M_{21}} & \mathbf{M_{22}} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) \\ \mathbf{T_2}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) \\ \vdots \end{pmatrix} \tag{104}$$

$\mathbf{T}^{\mathbf{T}}_{\mathbf{1}}(\mathbf{P}^{\dagger})$ and $\mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}})$ are property gradient vectors and are defined as:

$$\mathbf{T}^{\mathbf{T}}_{\mathbf{1}}(\mathbf{P}^{\dagger}) = \begin{pmatrix} {}^{\mathbf{e}}\mathbf{T}^{\mathbf{T}}_{\mathbf{1}}(\mathbf{P}^{\dagger}) & {}^{\mathbf{d}}\mathbf{T}^{\mathbf{T}}_{\mathbf{1}}(\mathbf{P}^{\dagger}) \end{pmatrix} \tag{105}$$

$$= \begin{pmatrix} \langle \Psi^{KS,(0)}|[\hat{\mathbf{q}}^{T}, \hat{P}]|\Psi^{KS,(0)}\rangle & \langle \Psi^{KS,(0)}|[(\hat{\mathbf{q}}^{\dagger})^{T}, \hat{P}]|\Psi^{KS,(0)}\rangle \end{pmatrix} \tag{106}$$

$$\mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) = \begin{pmatrix} {}^{\mathbf{e}}\mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) \\ {}^{\mathbf{d}}\mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) \end{pmatrix} = \begin{pmatrix} \langle \Psi^{KS,(0)}|[\hat{H}^{(1)}_{\omega,ext}, \hat{\mathbf{q}}^{\dagger}]|\Psi^{KS,(0)}\rangle \\ \langle \Psi^{KS,(0)}|[\hat{H}^{(1)}_{\omega,ext}, \hat{\mathbf{q}}]|\Psi^{KS,(0)}\rangle \end{pmatrix} \tag{107}$$

The $\mathbf{M_{11}}$ matrix element is the principal propagator matrix.

$$\mathbf{M_{11}} = \hbar\omega\mathbf{S_{11}} - \mathbf{E_{11}} \tag{108}$$

With the overlap matrix element $\mathbf{S_{11}}$ and the Hessian matrix element $\mathbf{E_{11}}$.

$$\mathbf{S_{11}} = \begin{pmatrix} {}^{\mathbf{ee}}\mathbf{S_{11}} & {}^{\mathbf{ed}}\mathbf{S_{11}} \\ {}^{\mathbf{de}}\mathbf{S_{11}} & {}^{\mathbf{dd}}\mathbf{S_{11}} \end{pmatrix} = \begin{pmatrix} \langle\Psi^{KS,(0)}|[\hat{\mathbf{q}},\hat{\mathbf{q}}^\dagger]|\Psi^{KS,(0)}\rangle & \langle\Psi^{KS,(0)}|[\hat{\mathbf{q}},\hat{\mathbf{q}}]|\Psi^{KS,(0)}\rangle \\ \langle\Psi^{KS,(0)}|[\hat{\mathbf{q}}^\dagger,\hat{\mathbf{q}}^\dagger]|\Psi^{KS,(0)}\rangle & \langle\Psi^{KS,(0)}|[\hat{\mathbf{q}}^\dagger,\hat{\mathbf{q}}]|\Psi^{KS,(0)}\rangle \end{pmatrix} \tag{109}$$

$$\mathbf{E_{11}} = \begin{pmatrix} {}^{\mathbf{ee}}\mathbf{E_{11}} & {}^{\mathbf{ed}}\mathbf{E_{11}} \\ {}^{\mathbf{de}}\mathbf{E_{11}} & {}^{\mathbf{dd}}\mathbf{E_{11}} \end{pmatrix} \tag{110}$$

$$\begin{aligned} {}^{\mathbf{ee}}\mathbf{E_{11}} = \langle\Psi^{KS,(0)}|[\hat{\mathbf{q}}^\dagger,[\hat{\mathbf{q}},\hat{H}^{KS,(0)}]]|\Psi^{KS,(0)}\rangle + \sum_{aibj}\langle\Psi^{KS,(0)}|[\hat{\mathbf{q}}^\dagger,\hat{E}_{ai}]|\Psi^{KS,(0)}\rangle \\ \times\left[\frac{1}{|\vec{r}\,'-\vec{r}|}+\frac{\delta\hat{v}_{XC}}{\delta\rho(\vec{r})}\right]_{aibj}\langle\Psi^{KS,(0)}|[\mathbf{q},\hat{E}_{bj}]|\Psi^{KS,(0)}\rangle \end{aligned} \tag{111}$$

$$\begin{aligned} {}^{\mathbf{ed}}\mathbf{E_{11}} = \langle\Psi^{KS,(0)}|[\hat{\mathbf{q}}^\dagger,[\hat{\mathbf{q}}^\dagger,\hat{H}^{KS,(0)}]]|\Psi^{KS,(0)}\rangle\sum_{aibj}\langle\Psi^{KS,(0)}|[\hat{\mathbf{q}}^\dagger,\hat{E}_{ai}]|\Psi^{KS,(0)})\rangle \\ \times\left[\frac{1}{|\vec{r}\,'-\vec{r}|}+\frac{\delta\hat{v}_{XC}}{\delta\rho(\vec{r})}\right]_{aibj}\langle\Psi^{KS,(0)}|[\mathbf{q}^\dagger,\hat{E}_{bj}]|\Psi^{KS,(0)}\rangle \end{aligned} \tag{112}$$

$$\begin{aligned} {}^{\mathbf{de}}\mathbf{E_{11}} = \langle\Psi^{KS,(0)}|[\hat{\mathbf{q}},[\hat{\mathbf{q}},\hat{H}^{KS,(0)}]]|\Psi^{KS,(0)}\rangle\sum_{aibj}\langle\Psi^{KS,(0)}|[\hat{\mathbf{q}},\hat{E}_{ai}]|\Psi^{KS,(0)}\rangle \\ \times\left[\frac{1}{|\vec{r}\,'-\vec{r}|}+\frac{\delta\hat{v}_{XC}}{\delta\rho(\vec{r})}\right]_{aibj}\langle\Psi^{KS,(0)}|[\mathbf{q},\hat{E}_{bj}]|\Psi^{KS,(0)}\rangle \end{aligned} \tag{113}$$

$$\begin{aligned} {}^{\mathbf{dd}}\mathbf{E_{11}} = \langle\Psi^{KS,(0)}|[\hat{\mathbf{q}},[\hat{\mathbf{q}}^\dagger,\hat{H}^{KS,(0)}]]|\Psi^{KS,(0)}\rangle\sum_{aibj}\langle\Psi^{KS,(0)}|[\hat{\mathbf{q}},\hat{E}_{ai}]|\Psi^{KS,(0)}\rangle \\ \times\left[\frac{1}{|\vec{r}\,'-\vec{r}|}+\frac{\delta\hat{v}_{XC}}{\delta\rho(\vec{r})}\right]_{aibj}\langle\Psi^{KS,(0)}|[\mathbf{q}^\dagger,\hat{E}_{bj}]|\Psi^{KS,(0)}\rangle \end{aligned} \tag{114}$$

The equation for the linear response function is exact, when all possible state transfer operators are included. The first-order polarization propagator approximation (FOPPA) includes only the one-electron state transfer operators, thus the expansion is no longer exact.[3] The FOPPA matrix equation can be written in terms of the

solution vector $\mathbf{X}(\omega)$.

$$\langle\langle \hat{P}_I(t); \hat{H}^{(1)}_{\omega}\rangle\rangle_{\omega} = \begin{pmatrix} {}^{\mathbf{e}}\mathbf{T}^{\mathbf{T}}_{\mathbf{1}}(\mathbf{P}^{\dagger}) & {}^{\mathbf{d}}\mathbf{T}^{\mathbf{T}}_{\mathbf{1}}(\mathbf{P}^{\dagger}) \end{pmatrix} \begin{pmatrix} {}^{\mathbf{e}}\mathbf{X}(\omega) \\ {}^{\mathbf{d}}\mathbf{X}(\omega) \end{pmatrix} \tag{115}$$

$$\begin{pmatrix} {}^{\mathbf{e}}\mathbf{X}(\omega) \\ {}^{\mathbf{d}}\mathbf{X}(\omega) \end{pmatrix} = \left[\hbar\omega \begin{pmatrix} {}^{\mathbf{ee}}\mathbf{S_{11}} & {}^{\mathbf{ed}}\mathbf{S_{11}} \\ {}^{\mathbf{de}}\mathbf{S_{11}} & {}^{\mathbf{dd}}\mathbf{S_{11}} \end{pmatrix} - \begin{pmatrix} {}^{\mathbf{ee}}\mathbf{E_{11}} & {}^{\mathbf{ed}}\mathbf{E_{11}} \\ {}^{\mathbf{de}}\mathbf{E_{11}} & {}^{\mathbf{dd}}\mathbf{E_{11}} \end{pmatrix} \right]^{-1} \begin{pmatrix} {}^{\mathbf{e}}\mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) \\ {}^{\mathbf{d}}\mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) \end{pmatrix} \tag{116}$$

Evaluation of the overlap matrices gives:

$${}^{\mathbf{ee}}\mathbf{S_{11}} = \langle \Psi^{KS,(0)} | [\hat{\mathbf{q}}, \hat{\mathbf{q}}^{\dagger}] | \Psi^{KS,(0)} \rangle = \langle \Psi^{KS,(0)} | \Psi^{KS,(0)} \rangle = 1 \tag{117}$$

$${}^{\mathbf{ed}}\mathbf{S_{11}} = \langle \Psi^{KS,(0)} | [\hat{\mathbf{q}}, \hat{\mathbf{q}}] | \Psi^{KS,(0)} \rangle = 0 \tag{118}$$

$${}^{\mathbf{de}}\mathbf{S_{11}} = \langle \Psi^{KS,(0)} | [\hat{\mathbf{q}}^{\dagger}, \hat{\mathbf{q}}^{\dagger}] | \Psi^{KS,(0)} \rangle = 0 \tag{119}$$

$${}^{\mathbf{dd}}\mathbf{S_{11}} = \langle \Psi^{KS,(0)} | [\hat{\mathbf{q}}^{\dagger}, \hat{\mathbf{q}}] | \Psi^{KS,(0)} \rangle = -{}^{\mathbf{ee}}\mathbf{S_{11}} = -1 \tag{120}$$

The electronic Hessian matrices can similar be evaluated, and the expressions are given later in this section. It is noted that the electronic Hessian is no longer exact, since only one-electron state transfer operators are used, thus the matrices are denoted differently. Noticing that ${}^{\mathbf{ee}}\mathbf{E_{11}} = ({}^{\mathbf{dd}}\mathbf{E_{11}})^*$ as well as ${}^{\mathbf{ed}}\mathbf{E_{11}} = ({}^{\mathbf{de}}\mathbf{E_{11}})^*$, and by using the new labels ${}^{\mathbf{ee}}\mathbf{E_{11}} = \mathbf{A}$ and ${}^{\mathbf{ed}}\mathbf{E_{11}} = \mathbf{B}$, the solution vector can be rewritten as:[3,25]

$$\begin{pmatrix} {}^{\mathbf{e}}\mathbf{X}(\omega) \\ {}^{\mathbf{d}}\mathbf{X}(\omega) \end{pmatrix} = \left[\hbar\omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} - \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \right]^{-1} \begin{pmatrix} {}^{\mathbf{e}}\mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) \\ {}^{\mathbf{d}}\mathbf{T_1}(\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}}) \end{pmatrix} \tag{121}$$

4 Explicit expressions for the A and B matrices

In order to derive the expressions for the $\mathbf{A}$ and $\mathbf{B}$ matrices and to interpret the solution vector $\mathbf{X}(\omega)$, one needs to consider the time-dependent KS equation and the orthonormality condition.

$$i\hbar\frac{\partial}{\partial t}|\varphi^{KS}_a(i,t,\vec{\mathcal{F}})\rangle = \hat{h}(\vec{r_i},t,\vec{\mathcal{F}})|\varphi^{KS}_a(i,t,\vec{\mathcal{F}}) \tag{122}$$

$$\langle\varphi_i^{KS}(i,t,\vec{\mathcal{F}})|\varphi_j^{KS}(i,t,\vec{\mathcal{F}})\rangle = \delta_{ij} \tag{123}$$

$\vec{\mathcal{F}}$ is included to indicate, that the time-dependent KS equation is solved iteratively with a perturbing field $\vec{\mathcal{F}}$ present. The field $\mathcal{F}$ is given by the dipole approximation:[3]

$$\mathcal{F}_\alpha(t) = \mathcal{F}_\alpha(\omega)cos(\omega t) = \frac{1}{2}\mathcal{F}_\alpha(\omega)(e^{i\omega t} + e^{-i\omega t}) \tag{124}$$

If assumed that any arbitrary variation of the wavefunction is allowed, then Frenkel's variational principle is equivalent to the time-dependent KS equation (Proof in appendix A), and one can write:[26,27]

$$\left(\hat{h}(\vec{r_i},t,\vec{\mathcal{F}}) - i\hbar\frac{\partial}{\partial t}\right)|\varphi_a^{KS}(i,t,\vec{\mathcal{F}})\rangle = \epsilon_a(\vec{\mathcal{F}})|\varphi_a^{KS}(i,t,\vec{\mathcal{F}})\rangle \tag{125}$$

The perturbed spinorbitals $\varphi_a^{KS}(i,t,\vec{\mathcal{F}})$ are then expanded in a set of unperturbed spinorbitals $\{\varphi_q^{KS}(i)\}$ obtained by solving the KS equation.[3]

$$\varphi_a^{KS}(i,t,\vec{\mathcal{F}}) = \sum_q^{all}\varphi_q^{KS}(i)U_{qa}(\vec{\mathcal{F}}) \tag{126}$$

$U_{qa}(\vec{\mathcal{F}})$ is the expansion coefficient. Inserting the expansion into eqn. (125) gives:

$$\left(\hat{h}(\vec{r_i},t,\vec{\mathcal{F}}) - i\hbar\frac{\partial}{\partial t}\right)\left|\sum_q^{all}\varphi_q^{KS}(i)U_{qa}(\vec{\mathcal{F}})\right\rangle = \epsilon_a(\vec{\mathcal{F}})\left|\sum_q^{all}\varphi_q^{KS}(i)U_{qa}(\vec{\mathcal{F}})\right\rangle \tag{127}$$

Left multiplication with another unperturbed spinorbital φ_p^{KS} and integration over all space yields:

$$\sum_q^{all}K_{pq}(\vec{\mathcal{F}})U_{qa}(\vec{\mathcal{F}}) = \epsilon_a(\vec{\mathcal{F}})\sum_q^{all}\delta_{pq}U_{qa}(\vec{\mathcal{F}}) \tag{128}$$

$K_{pq}(\vec{\mathcal{F}})$ being the time-dependent perturbed KS matrix:

$$K_{pq}(\vec{\mathcal{F}}) = \langle\varphi_p^{KS}(i)|\hat{h}(\vec{r_i},t,\vec{\mathcal{F}}) - i\hbar\frac{\partial}{\partial t}|\varphi_q^{KS}(i)\rangle \tag{129}$$

In the framework of perturbation theory, $K_{pq}(\vec{\mathcal{F}})$, $\epsilon_a(\vec{\mathcal{F}})$, and $U_{qa}(t,\vec{\mathcal{F}})$ are expanded in orders of the perturbing field.[3]

$$K_{pq}(\vec{\mathcal{F}}) = K_{pq}^{(0)} + \frac{1}{2}\sum_\alpha\mathcal{F}_\alpha(\omega)K_{\alpha,pq}^{(1)} + ... \tag{130}$$

$$\epsilon_a(\vec{\mathcal{F}}) = \epsilon_a^{(0)} + \frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)\epsilon_{\alpha,a}^{(1)} + ... \tag{131}$$

$$U_{qa}(\vec{\mathcal{F}}) = U_{qa}^{(0)} + \frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)U_{\alpha,qa}^{(1)} + ... \tag{132}$$

Considering terms up to first order, the equation becomes:

$$\sum_q^{all}\left(K_{pq}^{(0)}\frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)U_{\alpha,qa}^{(1)} + \frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)K_{\alpha,pq}^{(1)}U_{qa}^{(0)}\right)$$
$$= \epsilon_a^{(0)}\sum_q^{all}\delta_{pq}\frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)U_{\alpha,qa}^{(1)} + \frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)\epsilon_{\alpha,a}^{(1)}\sum_q^{all}\delta_{pq}U_{qa}^{(0)} \tag{133}$$

The equation can be reduced:

$$\sum_q^{all}\left(K_{pq}^{(0)}U_{\alpha,qa}^{(1)} + K_{\alpha,pq}^{(1)}U_{qa}^{(0)}\right) = \epsilon_a^{(0)}\sum_q^{all}\delta_{pq}U_{\alpha,qa}^{(1)} + \epsilon_{\alpha,a}^{(1)}\sum_q^{all}\delta_{pq}U_{qa}^{(0)} \tag{134}$$

The spinorbitals are similar expanded in orders of the perturbing field:

$$\varphi_a^{KS}(i,t,\vec{\mathcal{F}}) = \varphi_p^{KS}(i) + \frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)\varphi_r^{KS}(i)\left(U_{\alpha,rp}^{(1)}(\omega)e^{i\omega t} + U_{\alpha,rp}^{(1)}(-\omega)e^{-i\omega t}\right) + ... \tag{135}$$

$K_{pq}(\vec{\mathcal{F}})$ can then be written as:

$$K_{pq}(\vec{\mathcal{F}}) = \langle\varphi_p^{KS}(i)|\hat{h}(\vec{r_i},t,\vec{\mathcal{F}}) - i\hbar\frac{\partial}{\partial t}|\varphi_q^{KS}(i)\rangle \tag{136}$$

$$= \left\langle\varphi_p^{KS}(i) + \frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)\varphi_r^{KS}(i)\left(U_{\alpha,rp}^{(1)}(\omega)e^{i\omega t} + U_{\alpha,rp}^{(1)}(-\omega)e^{-i\omega t}\right)\right. \tag{137}$$

$$\times\left|\left\{(-\frac{1}{2})\hat{\nabla}_i^2 + \hat{v}_{ext}(\vec{r_i},t) + \int\frac{\rho(\vec{r_j},t)}{|\vec{r_i}-\vec{r_j}|}d\vec{r_j} + \frac{\delta\hat{v}_{XC}(\vec{r_i})}{\delta p(\vec{r_i})} - i\hbar\frac{\partial}{\partial t}\right\}\times\right. \tag{138}$$

$$\left.\left.\varphi_q^{KS}(i) + \frac{1}{2}\sum_\alpha \mathcal{F}_\alpha(\omega)\varphi_s^{KS}(i)\left(U_{\alpha,sq}^{(1)}(\omega)e^{i\omega t} + U_{\alpha,sq}^{(1)}(-\omega)e^{-i\omega t}\right)\right\rangle\right. \tag{139}$$

The unperturbed time-dependent KS matrix is identified as:

$$K_{pq}^{(0)}(\vec{\mathcal{F}}) = \langle\varphi_p^{KS}(i)|\Big\{-\frac{1}{2}\hat{\nabla}_i^2 + \hat{v}_{ext}(\vec{r_i},t) + \int\frac{\rho(\vec{r_j},t)}{|\vec{r_i}-\vec{r_j}|}d\vec{r_j} + \frac{\delta\hat{v}_{XC}(\vec{r_i})}{\delta p(\vec{r_i})}$$
$$- i\hbar\frac{\partial}{\partial t}\Big\}|\varphi_q^{KS}(i)\rangle = \epsilon_p^{(0)}\delta_{pq} \tag{140}$$

The first order perturbed time-dependent KS matrix is:

$$K_{pq}^{(1)}(\vec{\mathcal{F}}) = \left\langle \frac{1}{2}\sum_{\alpha}\mathcal{F}_{\alpha}(\omega)\varphi_r^{KS}(i)\left(U_{\alpha,rp}^{(1)}(\omega)e^{i\omega t} + U_{\alpha,rp}^{(1)}(-\omega)e^{-i\omega t}\right)\right| \tag{141}$$

$$\times\left\{(-\frac{1}{2})\hat{\nabla}_i^2 + \hat{v}_{ext}(\vec{r_i},t) + \int\frac{\rho(\vec{r_j},t)}{|\vec{r_i}-\vec{r_j}|}d\vec{r_j} + \frac{\delta\hat{v}_{XC}(\vec{r_i})}{\delta p(\vec{r_i})} - i\hbar\frac{\partial}{\partial t}\right\} \tag{142}$$

$$\times\left|\frac{1}{2}\sum_{\alpha}\mathcal{F}_{\alpha}(\omega)\varphi_s^{KS}(i)\left(U_{\alpha,sq}^{(1)}(\omega)e^{i\omega t} + U_{\alpha,sq}^{(1)}(-\omega)e^{-i\omega t}\right)\right\rangle \tag{143}$$

$$= \left\langle \frac{1}{2}\sum_{\alpha}\mathcal{F}_{\alpha}(\omega)\varphi_r^{KS}(i)U_{\alpha,rp}^{(1)}(\omega)e^{i\omega t}\right|\left\{ -\frac{1}{2}\hat{\nabla}_i^2 + \hat{v}_{ext}(\vec{r_i},t)\right. \tag{144}$$

$$\left. + \int\frac{\rho(\vec{r_j},t)}{|\vec{r_i}-\vec{r_j}|}d\vec{r_j} + \frac{\delta\hat{v}_{XC}(\vec{r_i})}{\delta p(\vec{r_i})} - i\hbar\frac{\partial}{\partial t}\right\}\left|\frac{1}{2}\sum_{\alpha}\mathcal{F}_{\alpha}(\omega)\varphi_s^{KS}(i)\right. \tag{145}$$

$$\left.\times U_{\alpha,sq}^{(1)}(\omega)e^{i\omega t}\right\rangle + c.c. \tag{146}$$

c.c. denotes the complex conjugate, and if assumed that the spinorbitals are real:

$$K_{pq}^{(1)}(\vec{\mathcal{F}}) = \left\langle \sum_{\alpha}\mathcal{F}_{\alpha}(\omega)\varphi_r^{KS}(i)U_{\alpha,rp}^{(1)}(\omega)e^{-i\omega t}\right|\left\{ -\frac{1}{2}\hat{\nabla}_i^2 + \hat{v}_{ext}(\vec{r_i},t)\right. \tag{147}$$

$$\left. + \int\frac{\rho(\vec{r_j},t)}{|\vec{r_i}-\vec{r_j}|}d\vec{r_j} + \frac{\delta\hat{v}_{XC}(\vec{r_i})}{\delta p(\vec{r_i})} - i\hbar\frac{\partial}{\partial t}\right\}\left|\sum_{\alpha}\mathcal{F}_{\alpha}(\omega)\varphi_s^{KS}(i)\right. \tag{148}$$

$$\left.\times U_{\alpha,sq}^{(1)}(\omega)e^{-i\omega t}\right\rangle \tag{149}$$

$$= \langle\varphi_p^{KS}(i)|\hat{H}_{ext}^{(1)}|\varphi_q^{KS}(i)\rangle + \sum_{j}^{occ}\sum_{tu}^{vir}\left(\mathcal{K}_{rs,tu} - \hbar\omega S_{rs}\right) \tag{150}$$

$$\times\left(U_{\alpha,tj}^{(1)}(\omega)\delta_{uj} + U_{\alpha,uj}^{(1),*}(\omega)\delta_{tj}\right) \tag{151}$$

$\mathcal{K}_{rs,tu}$ and S_{rs} are defined as:

$$\mathcal{K}_{rs,tu} = \langle\varphi_r^{KS}(i)\varphi_s^{KS}(j)|\left(\frac{1}{|\vec{r_i}-\vec{r_j}|} + \frac{\delta\hat{v}_{XC}(\vec{r_i})}{\delta p(\vec{r_i})}\right)|\varphi_t^{KS}(i)\varphi_u^{KS}(j)\rangle \tag{152}$$

$$S_{rs} = \delta_{rs} \tag{153}$$

The matrix containing the unperturbed expansions coefficients is diagonal.

$$U_{qa}^{(0)} = \delta_{qa} \tag{154}$$

Eqn. (134) is simplified by using the expression for the unperturbed KS matrix and the expansion coefficient matrix:

$$\epsilon_p^{(0)} U_{\alpha,pa}^{(1)} + K_{\alpha,pa}^{(1)} = \epsilon_a^{(0)} U_{\alpha,pa}^{(1)} + \epsilon_{\alpha,a}^{(1)} \delta_{qa} \tag{155}$$

$$\Leftrightarrow (\epsilon_p^{(0)} - \epsilon_a^{(0)}) U_{\alpha,pa}^{(1)} = \epsilon_{\alpha,a}^{(1)} \delta_{pa} - K_{\alpha,pa}^{(1)} \tag{156}$$

Assuming $p \neq a$, the parameterization of the matrix containing the first order expansion coefficients can be obtained:

$$U_{\alpha,pa}^{(1)} = \frac{-K_{\alpha,pa}^{(1)}}{\epsilon_p^{(0)} - \epsilon_a^{(0)}} \tag{157}$$

Inserting the expression for the first order perturbed time-dependent KS matrix and rearranging:

$$U_{\alpha,pa}^{(1)}(\epsilon_p^{(0)} - \epsilon_a^{(0)}) = -\Bigg(\langle \varphi_p^{KS}(i) | \hat{H}_{ext}^{(1)} | \varphi_a^{KS}(i) \rangle + \sum_j^{occ} \sum_{tu}^{vir} \Big(\mathcal{K}_{rs,tu} - \hbar\omega S_{rs} \Big) \times \Big(U_{\alpha,tj}^{(1)}(\omega) \delta_{uj} + U_{\alpha,uj}^{(1),*}(\omega) \delta_{tj} \Big) \Bigg) \tag{158}$$

$$\Leftrightarrow -\langle \varphi_p^{KS}(i) | \hat{H}_{ext}^{(1)} | \varphi_a^{KS}(i) \rangle = (\epsilon_p^{(0)} - \epsilon_a^{(0)}) \delta_{pq} \delta_{aj} + \sum_j^{occ} \sum_q^{vir} \Big(\mathcal{K}_{pa,qj} - \hbar\omega S_{rs} \Big) \times U_{\alpha,qj}^{(1)}(\omega) + \sum_j^{occ} \sum_q^{vir} \Big(\mathcal{K}_{pa,qj} - \hbar\omega S_{rs} \Big) U_{\alpha,qj}^{(1),*}(\omega) \tag{159}$$

The following two matrices are defined:[25,28]

$$A_{pa,qj} = (\epsilon_p^{(0)} - \epsilon_a^{(0)}) \delta_{pq} \delta_{aj} + \mathcal{K}_{pa,qj} \tag{160}$$

$$B_{pa,qj} = \mathcal{K}_{pa,qj} \tag{161}$$

The equation can then be written in a more compact form:

$$-\langle\varphi_p^{KS}(i)|\hat{H}_{ext}^{(1)}|\varphi_a^{KS}(i)\rangle = \sum_j^{occ}\sum_q^{vir}\Big(\big[A_{pa,qj}-\hbar\omega S_{rs}\big]U_{\alpha,qj}^{(1)}(\omega) + \big[B_{pa,qj}-\hbar\omega S_{rs}\big]U_{\alpha,qj}^{(1),*}(\omega)\Big) \quad (162)$$

If the perturbation is real (-ω), then $U_{\alpha,qj}^{(1),*} = U_{\alpha,qj}^{(1)}$, and if the perturbation is imaginary (+ω), then $U_{\alpha,qj}^{(1),*} = -U_{\alpha,qj}^{(1)}$.[3] Thus the equation can be rewritten:

$$-\langle\varphi_p^{KS}(i)|\hat{H}_{ext}^{(1)}|\varphi_a^{KS}(i)\rangle = \sum_j^{occ}\sum_q^{vir}\Big(\big[A_{pa,qj}-\hbar\omega S_{rs}\big] \mp \big[B_{pa,qj}-\hbar\omega S_{rs}\big]\Big) \times \big(\pm U_{\alpha,qj}^{(1)}(\omega)\big) \quad (163)$$

This can be written as a matrix equation:[3,25,28]

$$-\begin{pmatrix} {}^{e}\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}} \\ {}^{d}\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}} \end{pmatrix} = \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \hbar\omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix}\right] \begin{pmatrix} U_\alpha^{(1)}(-\omega) \\ -U_\alpha^{(1)}(\omega) \end{pmatrix} \quad (164)$$

$$\Leftrightarrow \left[\hbar\omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix} - \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}\right]^{-1} \begin{pmatrix} {}^{e}\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}} \\ {}^{d}\mathbf{H}^{(\mathbf{1})}_{\boldsymbol{\omega},\mathbf{ext}} \end{pmatrix} = \begin{pmatrix} U_\alpha^{(1)}(-\omega) \\ -U_\alpha^{(1)}(\omega) \end{pmatrix} \quad (165)$$

The matrices containing the expansions coefficients can be identified as the solution vectors:

$$\begin{pmatrix} U_\alpha^{(1)}(-\omega) \\ -U_\alpha^{(1)}(\omega) \end{pmatrix} = \begin{pmatrix} {}^{\mathbf{e}}\mathbf{X}(\omega) \\ {}^{\mathbf{d}}\mathbf{X}(\omega) \end{pmatrix} \quad (166)$$

For convenience, the transition vectors ${}^{\mathbf{e}}\mathbf{X}$ and ${}^{\mathbf{d}}\mathbf{X}$ are labeled $\mathbf{X}$ and $\mathbf{Y}$ respectively. Recalling that the vertical excitation energy is calculated as poles of the linear response function, the working equation for LR-TD-DFT can finally be stated:[28]

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \hbar\omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad (167)$$

5 Conclusion

We have formulated a new version of response theory namely the first-order polarization propagator approximation, and it is termed FOPPA. We have given a very detailed introduction to the method while utilizing the general framework of response theory. We have provided expressions for the matrix elements that enter when solving the matrix equations related to FOPPA. We have provided a presentation that will help new researchers to the gain and understanding of the underlying assumptions and tricks within response theory.

We plan to implement these equations in the electronic structure program Dalton QCP.[29,30] We have given a detailed derivation of the equations that form the basis for FOPPA, and thereby we have provided a guide for new researchers to enter the world of response theory. We hope that this detailed derivation will encourage new and young researchers to engage in the further developments of response theory.

6 Acknowledgement

7 References

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8 Appendix A

Frenkel's variational principle states:

$$\langle \delta\Psi | i\hbar \frac{\partial}{\partial t} - \hat{H}(t) | \Psi \rangle = 0 \tag{168}$$

Ψ is the many-electron wavefunction consisting of the spinorbitals $\{\varphi_i\}$ and $\hat{H}(t)$ is the sum of one-electron hamiltonians $\{\hat{h}_i(t)\}$. Assuming that any arbitrary variation of the wavefunction is allowed, then Frenkel's variational principle is equivalent to the time-dependent Schrödinger equation. If the variation of the wavefunction is given by:

$$|\delta\Psi\rangle = \epsilon(i\hbar \frac{\partial}{\partial t} - \hat{H}(t)|\Psi\rangle \tag{169}$$

ϵ being some parameter, and if the expectation value:

$$\langle \delta\Psi | \delta\Psi \rangle = 0 \tag{170}$$

Then we must have:

$$|\delta\Psi\rangle = \epsilon(i\hbar \frac{\partial}{\partial t} - \hat{H}(t)|\Psi\rangle = 0 \tag{171}$$

This can be rearranged to give the time-dependent Schrödinger equation.[27]

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H}(t)|\Psi\rangle \tag{172}$$

Now, if this is true, then the following must also be true.

$$\left(\hat{h}(t) - i\hbar\frac{\partial}{\partial t}\right)|\varphi_a\rangle = \epsilon_a|\varphi_a\rangle \tag{173}$$

Which validates the use of Frenkel's variational principle in eqn. (125). □