

# From Electrons to Materials Properties

Density Functional Theory for Engineers and Materials Scientists

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## **Chapter VIII**

# **Time-dependent Perturbations**

## Time-dependent DFT

We start with the time-dependent Hamiltonian

$$(1) \quad i \frac{\partial}{\partial t} \varphi_i(t, \mathbf{x}) = H[\rho] \varphi_i(t, \mathbf{x})$$

and write

$$(2) \quad H[\rho] = \frac{1}{2} \boldsymbol{\pi}^2(t, \mathbf{x}) + v[\rho](t, \mathbf{x})$$

Here, we have the generalized kinetic energy

$$(3) \quad \boldsymbol{\pi}(t, \mathbf{x}) = \mathbf{p}(t, \mathbf{x}) + \frac{A_{ext}(t, \mathbf{x})}{c}$$

and generalized potential energy

$$(4) \quad v[\rho](t, \mathbf{x}) = \int \frac{\rho(t, \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x}' + v_{xc}[\rho](t, \mathbf{x}) + v_{ext}(t, \mathbf{x})$$

The (external) perturbation potential consists of a scalar part

$$(5) \quad v_{ext}(t, \mathbf{x}) = v^{(0)}(\mathbf{x}) + \sum_{\alpha} \lambda_{\alpha} \left( v^{(\alpha)}(\omega_{\alpha}, \mathbf{x}) e^{i\omega_{\alpha}t} + v^{(\alpha)}(-\omega_{\alpha}, \mathbf{x}) e^{-i\omega_{\alpha}t} \right)$$

plus a vectorial part

$$(6) \quad \mathbf{A}_{ext}(t, \mathbf{x}) = \sum_{\alpha} \lambda_{\alpha} \left( \mathbf{A}^{(\alpha)}(\omega_{\alpha}, \mathbf{x}) e^{i\omega_{\alpha}t} + \mathbf{A}^{(\alpha)}(-\omega_{\alpha}, \mathbf{x}) e^{-i\omega_{\alpha}t} \right)$$

Here,  $\alpha$  denotes the order of the perturbational series expansion.

The good news is that the vector potential (eq. 6) yields a value of zero within the adiabatic approximation and the kinetic energy is not depending explicitly on time either.

For any transition from the ground state to the term of perturbation order  $\alpha$  we can map the transition density  $\gamma^{(\alpha)}$  from the Hilbert space  $L$ :

$$(7) \quad \gamma^{(\alpha)} \in L = L_{virt} \times L_{occ} \oplus L_{occ} \times L_{virt}$$

Applying a basis set expansion to the subspaces of occupied and unoccupied Kohn-Sham orbitals we obtain expansion coefficients for the transition density

$$(8) \quad \gamma^{(\alpha)}(\mathbf{x}, \mathbf{x}') = \sum_{a,r} \left( X_{ar}^{(\alpha)} \varphi_r(\mathbf{x}) \varphi_a(\mathbf{x}') + Y_{ar}^{(\alpha)} \varphi_a(\mathbf{x}) \varphi_r(\mathbf{x}') \right)$$

Instead of working with the full basis, we can (just as in HF and DFT) work with the expansion coefficients of this tensor space, i.e.

$$(9) \quad \begin{pmatrix} X \\ Y \end{pmatrix} = |X, Y\rangle$$

As long as we are dealing with a first-order perturbation we can simplify things. According to Rayleigh-Schrödinger perturbation theory, first-order properties can be derived from the unperturbed wavefunctions from our ground state

$$(10) \quad H[\rho]^{(0)}\varphi_i = \epsilon_i\varphi_i$$

We can compute the inner product of the expansion coefficients tensors as

$$(11) \quad \langle X_1, Y_1 | X_2, Y_2 \rangle = X_1^\dagger X_2 + Y_1^\dagger Y_2 = \sum_{ar} X_{1ar}^* X_{2ar} + Y_{1ar}^* Y_{2ar}$$

Introducing a matrix

$$(12) \quad \Delta = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}$$

allows us to orthonormalize these vectors.

Now let us solve the time-dependent perturbation equations. First, we introduce a matrix

$$(13) \quad \mathbf{\Lambda}(\omega) = \begin{pmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}(\omega) & \mathbf{A}(\omega) \end{pmatrix}$$

so that we can write an equation for first-order perturbed wavefunctions

$$(14) \quad (\mathbf{\Lambda}(\omega) - \omega\mathbf{\Delta})|X, Y\rangle = -|P, Q\rangle$$

The matrix blocks are defined as

$$(15) \quad (\mathbf{A}(\omega) - \mathbf{B}(\omega))_{arbs} = (\epsilon_r - \epsilon_a)\delta_{ab}\delta_{rs}$$

$$(16) \quad (\mathbf{A}(\omega) + \mathbf{B}(\omega))_{arbs} = (\mathbf{A}(\omega) - \mathbf{B}(\omega))_{arbs} + 2\mathbf{C}_{arbs}(\omega)$$

with

$$(17) \quad C_{ijkl} = \int \left( \varphi_i(\mathbf{x})\varphi_j(\mathbf{x}') \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\omega, \mathbf{x}, \mathbf{x}') \right) \right) \varphi_k(\mathbf{x})\varphi_l(\mathbf{x}') d\mathbf{x}$$

Considering the adiabatic approximation (Born-Oppenheimer approximation) to be valid, we obtain the time-dependent exchange-correlation functional

$$(18) \quad f_{xc}(\omega, \mathbf{x}, \mathbf{x}') = f_{xc}(0, \mathbf{x}, \mathbf{x}') = \left. \frac{\delta^2 E_{xc}(\rho)}{\delta\rho(\mathbf{x})\delta\rho(\mathbf{x}')} \right|_{\rho=\rho^{(0)}}$$

This means the XC functional is time-independent in first order!



Now we can already apply these results to a first problem. Consider we may want to know the dynamic polarizabilities of the electrons, i.e. in response to an electromagnetic field. The first thing we need to know is the dipole moment in the  $\alpha$ th state

$$(19) \quad |\mu_\alpha\rangle = \hat{\mu}|\alpha\rangle$$

Next, we can apply our perturbation straightforward and obtain

$$(20) \quad \alpha_{\alpha\beta}(\omega) = \langle \mu_\alpha | (\mathbf{\Lambda}(\omega) - \omega\mathbf{\Delta})^{-1} | \mu_\beta \rangle = - \langle X_\alpha, Y_\alpha | \mu_\beta \rangle$$

The only thing we need to define is our perturbation frequency  $\omega$  which is the frequency of our electromagnetic wave.

Beyond this, our transition densities yield poles at discrete frequencies, so that they solve the eigenfunction equation

$$(21) \quad (\mathbf{\Lambda}(\Omega_n) - \Omega_n \mathbf{\Delta}) |X_n, Y_n\rangle = 0$$

or

$$(22) \quad (\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B}) (X_n + Y_n) = \Omega_n^2 (X_n + Y_n)$$

The transition densities of different poles are orthonormal, so that for a single pole we obtain

$$(23) \quad \langle X_n, Y_n | \mathbf{\Delta} | X_n, Y_n \rangle = 1$$

Written in the basis, we obtain the transition density explicitly as

$$(24) \quad \gamma_n(\mathbf{x}, \mathbf{x}') = \sum_{a,r} (X_{nar} \varphi_r(\mathbf{x}) \varphi_a(\mathbf{x}') + Y_{nar} \varphi_a(\mathbf{x}) \varphi_r(\mathbf{x}'))$$

Using the transition dipole moment we obtain the oscillatory strength of the  $0 \leftarrow n$  transition as

$$(25) \quad f_{0n} = \frac{2}{3} \Omega_n |\langle \boldsymbol{\mu}_0 | \mathbf{X}_n, \mathbf{Y}_n \rangle|^2$$

Furthermore, we can compute an excited-state density functional

$$(26) \quad F[\mathbf{X}, \mathbf{Y}](\Omega_n, \mathbf{x}) = \langle \mathbf{X}, \mathbf{Y} | \Lambda(\Omega_n) | \mathbf{X}, \mathbf{Y} \rangle - \Omega (\langle \mathbf{X}, \mathbf{Y} | \Delta | \mathbf{X}, \mathbf{Y} \rangle - 1)$$

It allows us to derive the excited state electronic density

$$(27) \quad \rho_n = \frac{\partial F[\mathbf{X}, \mathbf{Y}](\Omega_n, \mathbf{x})}{\partial v_{ext}(0, \mathbf{x})}$$

or the excited state dipole moment

$$(28) \quad \boldsymbol{\mu}_n = \frac{\partial F[\mathbf{X}, \mathbf{Y}](\Omega_n, \mathbf{x})}{\partial \mathbf{E}}$$

While dealing with physical excitations, both matrices  $(\mathbf{A}+\mathbf{B})$  and  $(\mathbf{A}-\mathbf{B})$  are positive definite. If  $(\mathbf{A}+\mathbf{B})$  is indefinite, we are facing instabilities within the excited states, whereas with  $(\mathbf{A}-\mathbf{B})$  being indefinite the ground state is unstable. For instabilities, eq. 22 yields virtual eigenvalues for the excitation energy. In this case, most codes crash as virtual values are unphysical. If one still wants to continue, instead of the random phase approximation (RPA) discussed before one can switch to the Tamm-Dancoff approximation (TDA), which simplifies eq. 7 to

$$(29) \quad L = L_{virt} \times L_{occ}$$

This yields the easier eigenvalue equation

$$(30) \quad (\mathbf{A}(\Omega_n) - \Omega_n \mathbf{1})|\mathbf{X}_n\rangle = 0$$

Here, no virtual excitations can occur (but negative excitations may be observed – handle with caution!).

A note in the end: Eqs. 21, 22, 26, or 30 can be treated variationally.