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Time-dependent current-density-functional theory for molecules

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Chapter 1

Introduction to density functional theory

Prior to describing time-dependent density functional theory, we give a short overview of the ground state density functional theory (DFT) formalism. A recent fundamental overview of ground state DFT can be found in Ref. [28]. Books on this topic include Refs. [29] and [30].

1.1   Solving the Schrödinger equation

We would like to solve the time-independent Schrödinger equation for an isolated N-electron system in the Born-Oppenheimer nonrelativistic approximation, given by

$$\hat{H}\Psi\left(\mathbf{x}_1,\mathbf{x}_2,\dots,\mathbf{x}_N\right) = E\Psi\left(\mathbf{x}_1,\mathbf{x}_2,\dots,\mathbf{x}_N\right), \tag{1.1}$$

where E is the electronic energy, $\Psi\left(\mathbf{x}_1,\mathbf{x}_2,\dots,\mathbf{x}_N\right)$ is the N-electron wave function, and $\hat{H}$ is the Hamilton operator given by

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}. \tag{1.2}$$

In this equation $\hat{T}$ is the kinetic energy operator, $\hat{V}$ the external potential, and $\hat{W}$ the two-particle interaction. The coordinates $\mathbf{x}_i$ of electron i consist of space coordinates $\mathbf{r}_i$ and spin coordinate σ_i. Atomic units $\left(\hbar = m_e = e = 4\pi\varepsilon_0 = 1\right)$ will be used throughout this thesis. The separate terms of Eq. (1.2) are explicitly given by:

$$\hat{T} = \sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2\right) \tag{1.3}$$

$$\hat{V} = \sum_{i=1}^{N}\upsilon\left(\mathbf{r}_i\right) \tag{1.4}$$

$$\hat{W} = \sum_{i<j}^{N} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} , \qquad (1.5)$$

where the two-particle interaction $\hat{W}$ is the Coulomb potential. We define the density operator by,

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) . \qquad (1.6)$$

Eq. (1.4) can be written in terms of this density operator as:

$$\hat{V} = \int \upsilon(\mathbf{r}) \hat{\rho}(\mathbf{r}) d\mathbf{r} , \qquad (1.7)$$

its expectation value being:

$$\begin{aligned} \langle \Psi | \hat{V} | \Psi \rangle &= \int \Psi^* (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \hat{V} \Psi (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N \\ &= \int \rho(\mathbf{r}) \upsilon(\mathbf{r}) d\mathbf{r} \end{aligned} , \qquad (1.8)$$

where we have introduced the Dirac bracket notation. The last equation contains the electron density, which is the expectation value of the density operator

$$\begin{aligned} \rho(\mathbf{r}) &= \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle \\ &= N \int \left| \Psi (\mathbf{r}\sigma_1, \ldots, \mathbf{r}_N \sigma_N) \right|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N d\sigma_1 \ldots d\sigma_N \end{aligned} . \qquad (1.9)$$

When a system is in a state Ψ, which does not necessarily satisfies Eq. (1.1), the expectation value for the energy (i.e. the average of many measurements of the energy) is given by

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} . \qquad (1.10)$$

Since each measurement gives one of the eigenvalues of the Hamiltonian operator $\hat{H}$ it follows that

$$E[\Psi] \geq E_0 \qquad (1.11)$$

where E_0 is the energy of the ground state. Minimization of the *functional* $E[\Psi]$ will give a true ground state wave function Ψ_0 and energy $E[\Psi] = E_0$ (more information about functionals can be found in Appendix A). To ensure that the final Ψ will be normalized we use the method

of Lagrange multipliers in our minimization. Minimizing the quantity $\left[\langle\Psi|\hat{H}|\Psi\rangle - E\langle\Psi|\Psi\rangle\right]$ instead of just $\langle\Psi|\hat{H}|\Psi\rangle$, where E is the Lagrange multiplier, satisfies the constraint $\langle\Psi|\Psi\rangle = 1$. The Euler-Lagrange equations can be restated in a form that is equivalent to the Schrödinger equation where the Lagrange multipliers can be identified as the energy eigenvalues,

$$\delta E = \delta\langle\Psi|\hat{H}|\Psi\rangle - E\delta\langle\Psi|\Psi\rangle = 0 \, . \tag{1.12}$$

Note that the energy is now a functional of N and $\upsilon(\mathbf{r})$. Equation (1.12) must be solved for Ψ as a function of E, then E needs to be adjusted until normalization is achieved. This variational procedure is the starting point of many *ab initio* quantum chemical methods. These methods expand the wave function Ψ in a finite set of basis functions and use the variational procedure to find the coefficients of this expansion. Since it is usually not possible to work with a complete set of basis functions approximations need to be made. The simplest *ab initio* quantum chemical method is the Hartree-Fock approximation where one tries to find the best single Slater determinant that minimizes Eq. (1.10). Going beyond the ansatz of a single-determinant wave function can reduce the limitations of the Hartree-Fock method. Such approaches include many-body perturbation techniques and the linear mixing of many determinants (called configuration interaction) [31]. In the next section we discuss another quantum chemical method that has the electron density as the basic variable instead of the wave function, this method is density functional theory (DFT).

1.2 The Hohenberg-Kohn theorems

The advantage of DFT is that it is not necessary to calculate the complicated *N*-electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$. Instead one can restrict oneself to calculating the much simpler electron density $\rho(\mathbf{r})$, a fact that was first proven by Hohenberg and Kohn [1]. Their first Hohenberg-Kohn theorem states that the density $\rho(\mathbf{r})$ of a nondegenerate ground state uniquely determines the external potential $\upsilon(\mathbf{r})$ up to an arbitrary constant. From this theorem it follows that $\rho(\mathbf{r})$ determines the ground state wave function Ψ and through it all electronic properties. We proof this theorem in Appendix B.1. The consequence of the one-to-one mapping between the wave function Ψ and the density $\rho(\mathbf{r})$ is that the ground state density uniquely determines the expectation value of any operator $\hat{O}$

$$\langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle = O[\rho]. \qquad (1.13)$$

With this result we can define a universal Hohenberg-Kohn functional F_{HK}, which is independent of the potential $\hat{V}$, as

$$F_{HK}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \rangle \qquad (1.14)$$

and we find for the ground state energy functional $E_\upsilon[\rho]$

$$E_\upsilon[\rho] = \int \rho(\mathbf{r}) \upsilon(\mathbf{r}) d\mathbf{r} + F_{HK}[\rho]. \qquad (1.15)$$

The second Hohenberg-Kohn theorem states that for a trial density $\tilde{\rho}(\mathbf{r})$ such that $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$,

$$E_0 = E_{\upsilon_0}[\rho_0] \leq E_{\upsilon_0}[\tilde{\rho}]. \qquad (1.16)$$

This is the analogue of the variational principle for wave functions. This means that the exact ground state energy can be found by minimization of the energy functional

$$E_0 = \min_{\tilde{\rho}} E_{\upsilon_0}[\tilde{\rho}]. \qquad (1.17)$$

An important point within DFT that we have not addressed up to now is the so-called υ-representability problem. A density is defined to be υ-representable if it is the density associated with the anti-symmetric ground-state wave function of a Hamiltonian of the form (1.2) with some external potential υ. The functional F_{HK}, for example, is only defined on the set of υ-representable densities. The υ-representability problem deals with the question of what constraints one has to put on the density to make sure it is υ-representable. This problem is discussed in more detail in Refs. [30] and [32]. In the following we will assume our densities to be υ-representable.

1.3   The Kohn-Sham equations

While the Hohenberg-Kohn theorem shows it is possible to use the ground state density to calculate properties of the system, it does not provide a way of finding the ground state density. Kohn and Sham provided a route to this [2]. The practical scheme that Kohn and Sham devised is based on a hypothetical system of noninteracting electrons, chosen in such a way that the density of this system is identical to the exact density of the physical system under

consideration. It also reintroduces the concept of orbitals into the theory as we shall later see. An elegant way to derive these so-called Kohn-Sham equations is by means of Legendre transforms as derived by Van Leeuwen [28], which we give here. A more traditional way of deriving these equations is by means of the Euler-Lagrange equation as can be found in many textbooks on this subject (for example Refs. [29] and [30]).

We start our derivation with the Schrödinger equation,

$$\left(\hat{T} + \hat{V} + \hat{W}\right)\big|\Psi[v]\big\rangle = E[v]\big|\Psi[v]\big\rangle, \tag{1.18}$$

where the ground state energy $E[v]$ and the wave function $\Psi[v]$ are considered to be functionals of the external potential and the two-particle interaction $\hat{W}$ is kept fixed. Instead of this equation we can also write,

$$E[v] = \big\langle\Psi[v]\big|\hat{H}\big|\Psi[v]\big\rangle. \tag{1.19}$$

The goal is to go from the potential as the basic variable to the electron density. The reason why this is possible is that the density and the potential are conjugate variables, which means that the contribution of the external potential to the total energy occurs only via an integral of the potential times the density. We can now take the *functional derivative* (see appendix A for the definition) of the energy functional $E[v]$ with respect to the potential v,

$$\begin{aligned}\frac{\delta E}{\delta v(\mathbf{r})} &= \left\langle\frac{\partial\Psi}{\delta v(\mathbf{r})}\bigg|\hat{H}\big|\Psi\right\rangle + \left\langle\Psi\big|\hat{H}\bigg|\frac{\partial\Psi}{\delta v(\mathbf{r})}\right\rangle + \left\langle\Psi\bigg|\frac{\delta\hat{H}}{\delta v(\mathbf{r})}\big|\Psi\right\rangle \\ &= E[v]\frac{\delta}{\delta v(\mathbf{r})}\langle\Psi|\Psi\rangle + \langle\Psi|\hat{\rho}(\mathbf{r})|\Psi\rangle \\ &= \langle\Psi|\hat{\rho}(\mathbf{r})|\Psi\rangle = \rho(\mathbf{r})\end{aligned} \tag{1.20}$$

where we made explicit use of the fact that $\Psi[v]$ satisfies the Schrödinger equation with $\hat{H} = \hat{H}[v]$ as well as the normalization condition $\langle\Psi|\Psi\rangle = 1$, and that the external potential is defined as in Eq. (1.7). To go to the density as the basic variable we can use the technique of Legendre transforms. We can define the following Legendre transforms,

$$F[\rho] = E[v] - \int\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} = \big\langle\Psi[v]\big|\hat{T} + \hat{W}\big|\Psi[v]\big\rangle, \tag{1.21}$$

where v should now be regarded as a functional of ρ. We have already shown that the uniqueness of the mapping between v and ρ is guaranteed by the first Hohenberg-Kohn theorem.

Again $F[\rho]$ is only defined for the set of υ-representable densities, but as mentioned before we assume all our densities are υ-representable. Using the relation derived in Eq. (1.20) it follows that,

$$
\begin{aligned}
\frac{\delta F}{\delta \rho(\mathbf{r})} &= \int \frac{\delta E}{\delta \upsilon(\mathbf{r}')} \frac{\delta \upsilon(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}' - \frac{\delta}{\delta \rho(\mathbf{r})} \int \rho(\mathbf{r}') \upsilon(\mathbf{r}') d\mathbf{r}' \\
&= \int \rho(\mathbf{r}') \frac{\delta \upsilon(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}' - \int \rho(\mathbf{r}') \frac{\delta \upsilon(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r} - \int \frac{\delta \rho(\mathbf{r}')}{\delta \rho(\mathbf{r})} \upsilon(\mathbf{r}') d\mathbf{r} . \\
&= -\int \delta(\mathbf{r}' - \mathbf{r}) \upsilon(\mathbf{r}') d\mathbf{r}' = -\upsilon(\mathbf{r})
\end{aligned}
\tag{1.22}
$$

As mentioned above we consider a system of noninteracting particles in order to derive the Kohn-Sham equations. Analogous to the hypothetical system described above, we can write the following energy functional for this system with effective external potential υ_s and noninteracting wave function $|\Phi[\upsilon_s]\rangle$,

$$
E_s[\upsilon_s] = \langle \Phi[\upsilon_s] | \hat{T} + \hat{V}_s | \Phi[\upsilon_s] \rangle ,
\tag{1.23}
$$

with Legendre transform,

$$
F_s[\rho] = E_s[\upsilon_s] - \int \rho(\mathbf{r}) \upsilon_s(\mathbf{r}) d\mathbf{r} = \langle \Phi[\upsilon_s] | \hat{T} | \Phi[\upsilon_s] \rangle
\tag{1.24}
$$

and derivatives

$$
\frac{\delta E_s}{\delta \upsilon_s(\mathbf{r})} = \rho(\mathbf{r})
\tag{1.25}
$$

$$
\frac{\delta F_s}{\delta \rho(\mathbf{r})} = -\upsilon_s(\mathbf{r}) .
\tag{1.26}
$$

The $F_s[\rho]$ in equation (1.24) is nothing more than the kinetic energy of the noninteracting system. Therefore we will from now on denote this quantity by $T_s[\rho]$. We can now define the so-called exchange-correlation functional $E_{\mathrm{xc}}[\rho]$ by,

$$
F[\rho] = T_s[\rho] + \tfrac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\mathrm{xc}}[\rho] .
\tag{1.27}
$$

Here we assume that the noninteracting system is chosen such that its density corresponds with the ground state density of the interacting system. Functional differentiating Eq. (1.27) with respect to the density $\rho(\mathbf{r})$ gives,

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}), \qquad (1.28)$$

where,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \qquad (1.29)$$

defines the exchange-correlation potential. We can write the ground state wave function of a nondegenerate noninteracting system $|\Phi[v_s]\rangle$ as the antisymmetrized product of single particle orbitals $\phi_i(\mathbf{r})$ (i.e. a Slater determinant). Combining Eqs. (1.21) and (1.27) we obtain,

$$\begin{aligned} E[v] = &-\frac{1}{2} \sum_{i=1}^{N} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \\ &+ \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] \end{aligned} \qquad (1.30)$$

We also obtain a one-particle Schrödinger equation,

$$\left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \qquad (1.31)$$

and

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 . \qquad (1.32)$$

Equations (1.30), (1.31), and (1.32) constitute the ground state Kohn-Sham equations [2]. These equations reduce the problem of finding the ground state density to finding a good approximation for the exchange-correlation energy. Since $v_s(\mathbf{r})$ depends on $\rho(\mathbf{r})$ the equations need to be solved self-consistently. From a guessed density one can obtain $v_s(\mathbf{r})$ and then find a new $\rho(\mathbf{r})$ from (1.31) and (1.32). One can then continue the cycle by finding a new $v_s(\mathbf{r})$ from this density and continue until self-consistency is reached.

1.4   Approximate exchange-correlation functionals

The simplest approximation one can make for the exchange-correlation energy is the local density approximation (LDA). In this approximation the exchange-correlation energy functional is given by

$$E_{\mathrm{xc}}^{\mathrm{LDA}}\left[\rho\right] = \int \rho(\mathbf{r})\varepsilon_{\mathrm{xc}}^{\mathrm{hom.}}\left(\rho(\mathbf{r})\right)d\mathbf{r}\,, \tag{1.33}$$

where $\varepsilon_{\mathrm{xc}}^{\mathrm{hom.}}\left(\rho\right)$ is the exchange-correlation energy per particle for a homogeneous electron gas evaluated at the local density $\rho(\mathbf{r})$. In this way the system is treated locally as a homogeneous electron gas. It would be expected that this approximation would only be successful for systems with a slowly varying density, but is turns out that the LDA is very successful even for very inhomogeneous systems such as atoms and molecules. The functional $\varepsilon_{\mathrm{xc}}^{\mathrm{hom.}}\left(\rho\right)$ can be split into an exchange and a correlation part. The exchange part is given by the Dirac exchange-energy functional [33],

$$\varepsilon_{\mathrm{x}}\left(\rho\right) = -\frac{3}{4}\left(\frac{3}{\pi}\rho\right)^{1/3}\,. \tag{1.34}$$

Accurate values for the correlation part $\varepsilon_{\mathrm{c}}\left(\rho\right)$ have been obtained by quantum Monte-Carlo calculations and have been fitted to analytical functions. The parameterization of Vosko, Wilk, and Nusair (VWN) [34] is implemented in many quantum chemical codes. Even though the LDA is successful, it has many shortcomings. For example, it neglects all nonlocal effects. It is therefore not to be expected that the LDA works in cases where the density varies strongly. Also the exchange part of the functional does not exactly cancel the self-energy part of the Hartree term, which leads to incorrect asymptotic behavior for finite systems.

Including gradients of the density in the functional can make a considerable improvement upon the LDA. A successful way to construct these gradient expanded functionals is by use of the generalized gradient approximation (GGA) [35-37]. These GGA functionals can be written as,

$$E_{\mathrm{xc}}^{\mathrm{GGA}}\left[\rho\right] = \int \rho(\mathbf{r})\varepsilon_{\mathrm{xc}}^{\mathrm{GGA}}\left(\rho(\mathbf{r}),\nabla\rho(\mathbf{r})\right)d\mathbf{r}\,. \tag{1.35}$$

The function $\varepsilon_{\mathrm{xc}}^{\mathrm{GGA}}$ is usually an analytic function with parameters that are fitted to experiment or determined by exact sum rules. The GGAs already give accurate results for many properties and systems. A newer class of GGAs are the meta-GGAs [38] that depend explicitly on the

kinetic energy density of the Kohn-Sham system. These more flexible functionals are not only dependent on the density but also on the Kohn-Sham orbitals. The GGAs and meta-GGAs improve upon the LDA but they still do not have the correct asymptotic behavior. Van Leeuwen and Baerends proposed a density functional that does have the correct asymptotic behavior [39]. Another density functional that has a correct asymptotic behavior is developed with the method of statistical averaging of (model) orbital potentials (SAOP) [40]. This potential is especially constructed for the calculation of molecular response properties and its shape reflects the atomic shell structure.

Many more functionals have been developed, and the development of more accurate functionals is an ongoing process.