An Introduction to First-Principles Electron Dynamics Calculations Based on Time-Dependent Density Functional Theory

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Preface

These notes were prepared for students conducting research in the Sato Group of the Condensed Matter Theory Laboratory, Graduate School of Science, Tohoku University, with the aim of introducing the fundamentals of first-principles electron dynamics calculations based on time-dependent density functional theory. They are also intended to provide a first exposure to practical density functional theory and time-dependent density functional theory calculations for simple molecules and solids using first-principles simulation software, thereby serving as preparation for theoretical studies of light–matter interactions. These notes are still in draft form, and their contents are updated from time to time. For the latest version, please consult the note at the URL below.

`https://shunsuke-sato.github.io/page/etc/lecture_notes/LectureNoteForTDDFT_en.pdf`

1 Introduction: Time-Dependent Schrödinger Equation for Many-Electron Systems

In these notes, we consider first-principles electron dynamics calculations based on time-dependent density functional theory (TDDFT). The starting point is the many-body time-dependent Schrödinger equation that governs the time evolution of a many-electron system. In this section, we first review the form of this exact many-body problem and clarify which quantities must be specified in order to determine the time evolution. This serves as preparation for introducing TDDFT in the next section, where the density is taken as the basic variable.

The main object considered in these notes is a quantum many-body system described by the time-dependent Schrödinger equation for an N-particle system of the form

$$i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t)=\hat{H}(t)\Psi(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t), \tag{1}$$

$$\hat{H}(t)=\sum_{j=1}^{N}\left[\frac{\boldsymbol{p}_j^2}{2m}+v(\boldsymbol{r}_j,t)\right]+\frac{1}{2}\sum_{j\neq k}w(|\boldsymbol{r}_j-\boldsymbol{r}_k|). \tag{2}$$

Here, $\boldsymbol{r}_j$ denotes the position of the jth particle, and σ_j its spin coordinate. In addition, $v(\boldsymbol{r},t)$ is the external one-body potential, and $w(r)$ is the two-body interaction potential.

For the many-electron systems we have in mind, these potentials may, for example, be taken as

$$v(\boldsymbol{r},t)=-\frac{e^2}{4\pi\epsilon_0}\sum_a\frac{Z_a}{|\boldsymbol{r}-\boldsymbol{R}_a(t)|}-e\phi_{\text{ext}}(\boldsymbol{r},t), \tag{3}$$

$$w(r)=\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}. \tag{4}$$

Here, Z_a and $\boldsymbol{R}_a(t)$ denote the nuclear charge and position of the ath nucleus, respectively, and $\phi_{\text{ext}}(\boldsymbol{r},t)$ is a time-dependent external electromagnetic scalar potential. With the one-body and two-body potentials specified in this way, Eq. (1) describes the dynamics of an N-electron system moving under the Coulomb potential generated by the nuclei and the external electromagnetic scalar potential.

In principle, if Eq. (1) could be solved directly, one would obtain a detailed description of the dynamics of an electron system driven by an external potential. Through such an analysis, one could also describe theoretically a wide variety of physical phenomena arising from light–matter interactions. In practice, however, solving the many-body Schrödinger equation directly is generally extremely difficult. The reason is that, as the number of particles increases, the dimension of the space in which the wavefunction is defined grows exponentially.

We therefore regard Eq. (1) as an initial-value problem. Let the wavefunction at the initial time $t=t_0$ be

$$\Psi(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t_0)=\Psi_0(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N) \tag{5}$$

Further, throughout these notes we assume the following two points.

- The two-body interaction $w(r)$ is given in advance and cannot be changed arbitrarily. For example, in an electronic system, $w(r)$ is the Coulomb interaction itself, and it is not something that can be modified.
- The external one-body potential $v(\boldsymbol{r},t)$ is specified separately for each problem. For example, when one wishes to control an electron system by irradiating it with electromagnetic waves, $v(\boldsymbol{r},t)$ must be chosen appropriately according to the physical problem under consideration.

From this viewpoint, since the two-body interaction $w(r)$ is fixed, the quantities that must be specified for each problem are the initial wavefunction $\Psi_0(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N)$ and the one-body potential $v(\boldsymbol{r}, t)$. Once these are given, the physical problem is completely defined, and solving Eq. (1) uniquely determines the time-dependent many-body wavefunction $\Psi(\boldsymbol{r}_1, \sigma_1, \cdots, \boldsymbol{r}_N, \sigma_N, t)$. Writing this as

$$\Psi(\boldsymbol{r}_1, \sigma_1, \cdots, \boldsymbol{r}_N, \sigma_N, t) = \Psi\left[\Psi_0(\boldsymbol{r}_1, \sigma_1, \cdots, \boldsymbol{r}_N, \sigma_N), v(\boldsymbol{r}, t)\right](\boldsymbol{r}_1, \sigma_1, \cdots, \boldsymbol{r}_N, \sigma_N, t)$$

shows that the many-body wavefunction is a functional of the initial wavefunction $\Psi_0(\boldsymbol{r}_1, \sigma_1, \cdots, \boldsymbol{r}_N, \sigma_N)$ and the one-body potential $v(\boldsymbol{r}, t)$. Moreover, if the wavefunction is a functional of these quantities, then any physical observable computed from it can likewise be expressed as a functional of the same quantities. This viewpoint leads directly to the basic idea of time-dependent density functional theory discussed in the next section. Note also that, in the present problem, once the one-body potential at the initial time ($t = t_0$) is specified, the many-body Hamiltonian [Eq. (2)] is fixed. Its ground state is then a functional of the one-body potential at the initial time. In many problems, the initial wavefunction is taken to be this ground state. Therefore, if one restricts the initial condition to the ground state, the many-body wavefunction $\Psi(\boldsymbol{r}_1, \sigma_1, \cdots, \boldsymbol{r}_N, \sigma_N, t)$ may be regarded as a functional of the one-body potential $v(\boldsymbol{r}, t)$ alone, and all physical observables likewise become functionals of $v(\boldsymbol{r}, t)$.

2 Fundamentals of Time-Dependent Density Functional Theory

In the previous section, we confirmed that once the initial wavefunction and the one-body potential are given, the time evolution of the many-body system is uniquely determined. In this section, we introduce the basic idea of time-dependent density functional theory (TDDFT), which replaces the description in terms of the wavefunction by one in terms of the particle density. We first explain, through the Runge–Gross theorem, why the density can be adopted as the basic variable, and then introduce the Kohn–Sham mapping that connects this idea to practical calculations.

2.1 Runge–Gross theorem

In density functional theory (DFT) for ground states, the Hohenberg–Kohn theorem, which establishes a one-to-one correspondence between the one-body potential and the ground-state density, plays a central role. The counterpart for time-dependent problems is the Runge–Gross theorem. It states that, for a fixed initial state, there is a one-to-one correspondence between the one-body potential $v(\boldsymbol{r},t)$ and the particle density $\rho(\boldsymbol{r},t)$. Therefore, the density can be used as a basic variable in place of the wavefunction.

In what follows, we assume that the many-body wavefunction $\Psi(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t)$ is normalized, and define the particle density $\rho(\boldsymbol{r},t)$ and the current density $\boldsymbol{j}(\boldsymbol{r},t)$ by

$$\rho(\boldsymbol{r},t) = N \sum_{\sigma_1,\cdots,\sigma_N} \int d\boldsymbol{r}_2\cdots d\boldsymbol{r}_N \left|\Psi(\boldsymbol{r},\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t)\right|^2, \tag{6}$$

$$\boldsymbol{j}(\boldsymbol{r},t) = N \sum_{\sigma_1,\cdots,\sigma_N} \mathrm{Re}\left[\int d\boldsymbol{r}_2\cdots d\boldsymbol{r}_N\, \Psi^*(\boldsymbol{r},\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t)\frac{\boldsymbol{p}}{m}\Psi(\boldsymbol{r},\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t)\right] \tag{7}$$

Here, $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$ is the momentum operator acting on the coordinate $\boldsymbol{r}$. These quantities satisfy the continuity equation expressing particle-number conservation:

$$\frac{\partial}{\partial t}\rho(\boldsymbol{r},t) + \boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t) = 0 \tag{8}$$

As in the previous section, we assume that the two-body interaction $w(r)$ is fixed and that the many-body wavefunction evolves in time according to Eq. (1). Let the initial condition at time $t = t_0$ be written as

$$\Psi(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t_0) = \Psi_0(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N) \tag{9}$$

Since the initial wavefunction Ψ_0 and the two-body interaction $w(r)$ are fixed, the only quantity that can be chosen freely from one problem to another is the one-body potential $v(\boldsymbol{r},t)$.

The content of the Runge–Gross theorem is that, under these conditions, a one-to-one correspondence holds between the one-body potential $v(\boldsymbol{r},t)$ and the density $\rho(\boldsymbol{r},t)$.[1] Below, assuming that the potential is Taylor expandable in the neighborhood of $t = t_0$, we follow the outline of the proof.

First, consider two potentials $v(\boldsymbol{r},t)$ and $v'(\boldsymbol{r},t)$ that do not coincide up to a function of time alone. That is,

$$v(\boldsymbol{r},t) - v'(\boldsymbol{r},t) \neq C(t) \tag{10}$$

Then there exists a smallest nonnegative integer k satisfying

$$\frac{\partial^k}{\partial t^k}\left[v(\boldsymbol{r},t) - v'(\boldsymbol{r},t)\right]\Big|_{t=t_0} \neq \text{const.} \tag{11}$$

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[1] Here, potentials that differ only by a function of time are regarded as identical.

Since the two systems start from the same initial wavefunction Ψ_0 and share the same two-body interaction, the time derivative of the difference between their current densities satisfies

$$\frac{\partial}{\partial t}\left[\boldsymbol{j}(\boldsymbol{r},t)-\boldsymbol{j}'(\boldsymbol{r},t)\right]=-\frac{1}{m}\left[\rho(\boldsymbol{r},t)\boldsymbol{\nabla}v(\boldsymbol{r},t)-\rho'(\boldsymbol{r},t)\boldsymbol{\nabla}v'(\boldsymbol{r},t)\right] \tag{12}$$

Furthermore, differentiating both sides k times with respect to t and using the fact that the two wavefunctions coincide with the initial condition in Eq. (9) at $t=t_0$, we obtain

$$\frac{\partial^{k+1}}{\partial t^{k+1}}\left[\boldsymbol{j}(\boldsymbol{r},t)-\boldsymbol{j}'(\boldsymbol{r},t)\right]\Big|_{t=t_0}=-\frac{\rho(\boldsymbol{r},t_0)}{m}\boldsymbol{\nabla}\frac{\partial^k}{\partial t^k}\left[v(\boldsymbol{r},t)-v'(\boldsymbol{r},t)\right]\Big|_{t=t_0}\neq 0 \tag{13}$$

Therefore, if the two potentials are different, the corresponding current densities must also differ for $t>t_0$.

Next, differentiate the density difference $\rho(\boldsymbol{r},t)-\rho'(\boldsymbol{r},t)$ $(k+2)$ times with respect to t. Using Eq. (8) together with Eq. (13), one finds

$$\frac{\partial^{k+2}}{\partial t^{k+2}}\left[\rho(\boldsymbol{r},t)-\rho'(\boldsymbol{r},t)\right]\Big|_{t=t_0}=\frac{1}{m}\boldsymbol{\nabla}\cdot\left(\rho(\boldsymbol{r},t_0)\boldsymbol{\nabla}\frac{\partial^k}{\partial t^k}\left[v(\boldsymbol{r},t)-v'(\boldsymbol{r},t)\right]\Big|_{t=t_0}\right) \tag{14}$$

Thus, if one can show that the right-hand side of Eq. (14) is nonzero, it follows that two different potentials give rise to two different densities.

To this end, suppose that for a function $u(\boldsymbol{r})\neq$ const.,

$$\boldsymbol{\nabla}\cdot\left(\rho(\boldsymbol{r},t_0)\boldsymbol{\nabla}u(\boldsymbol{r})\right)=0 \tag{15}$$

holds. Multiplying by $u(\boldsymbol{r})$, integrating over space, and performing integration by parts, we obtain

$$\begin{aligned}0&=\int d\boldsymbol{r}\,u(\boldsymbol{r})\boldsymbol{\nabla}\cdot\left(\rho(\boldsymbol{r},t_0)\boldsymbol{\nabla}u(\boldsymbol{r})\right)\\&=-\int d\boldsymbol{r}\,\rho(\boldsymbol{r},t_0)\left|\boldsymbol{\nabla}u(\boldsymbol{r})\right|^2+\frac{1}{2}\int_S d\boldsymbol{S}\cdot\rho(\boldsymbol{r},t_0)\boldsymbol{\nabla}u^2(\boldsymbol{r})\end{aligned} \tag{16}$$

If the initial density $\rho(\boldsymbol{r},t_0)$ decays sufficiently rapidly at large distances, the surface integral vanishes. One then obtains $\rho(\boldsymbol{r},t_0)\left|\boldsymbol{\nabla}u(\boldsymbol{r})\right|^2=0$, which contradicts $u(\boldsymbol{r})\neq$ const.. Therefore,

$$\boldsymbol{\nabla}\cdot\left(\rho(\boldsymbol{r},t_0)\boldsymbol{\nabla}u(\boldsymbol{r})\right)\neq 0 \tag{17}$$

and hence the right-hand side of Eq. (14) is nonzero. It follows that densities evolving under different potentials must necessarily be different.

We have thus shown that, when time evolution is generated from a given initial wavefunction, there is a one-to-one correspondence between the one-body potential $v(\boldsymbol{r},t)$ and the density $\rho(\boldsymbol{r},t)$. This is the Runge–Gross theorem, which provides the starting point of TDDFT. Combined with the discussion in the previous section, it implies that the many-body wavefunction

$$\Psi\left[\Psi_0(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N),v(\boldsymbol{r},t)\right](\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t)$$

can also be expressed as a functional of the initial wavefunction Ψ_0 and the density $\rho(\boldsymbol{r},t)$:

$$\Psi\left[\Psi_0(\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N),\rho(\boldsymbol{r},t)\right](\boldsymbol{r}_1,\sigma_1,\cdots,\boldsymbol{r}_N,\sigma_N,t)$$

Therefore, any physical quantity can be described as a functional of the initial wavefunction Ψ_0 and the density $\rho(\boldsymbol{r},t)$.

Moreover, in many applications the initial wavefunction is taken to be the ground state of the initial Hamiltonian. In that case, the Hohenberg–Kohn theorem implies a one-to-one correspondence between the one-body potential $v(\boldsymbol{r},t_0)$ at the initial time $t=t_0$ and the ground-state density $\rho_{\mathrm{gs}}(\boldsymbol{r})$. Hence, the initial wavefunction itself may be regarded as a functional of the initial density, and the many-body wavefunction can then be treated as a functional of the density $\rho(\boldsymbol{r},t)$ alone. This is the reason why the density is adopted as the basic variable in TDDFT.

2.2 Kohn–Sham Mapping and the Time-Dependent Kohn–Sham Equation

The Runge–Gross theorem tells us that a many-body system can be described using the density as its basic variable. By itself, however, this theorem does not yet tell us how to compute the time evolution of an interacting many-body system in practice. What makes TDDFT a practical computational method is the Kohn–Sham mapping, which maps an interacting system onto a noninteracting one while preserving the density.

Let us call the original many-body system of interest the **interacting system**. It is specified by the initial state $|\Psi_0\rangle$, the one-body potential $v(\boldsymbol{r}, t)$, and the two-body interaction $w(r)$, and its density is denoted by $\rho(\boldsymbol{r}, t)$. In contrast, we introduce a noninteracting system with the same number of particles and call it the **Kohn–Sham system**. In the Kohn–Sham system, each particle moves under an effective one-body potential $v_{\mathrm{KS}}(\boldsymbol{r}, t)$, and its density is denoted by $\rho_{\mathrm{KS}}(\boldsymbol{r}, t)$.

The basic idea of TDDFT is to construct a Kohn–Sham system that yields the same density as the interacting system. That is, we consider a noninteracting system such that $\rho_{\mathrm{KS}}(\boldsymbol{r}, t) = \rho(\boldsymbol{r}, t)$. Strictly speaking, the initial state $|\Phi_0\rangle$ of the Kohn–Sham system must be chosen so that not only the initial density $\rho(\boldsymbol{r}, t_0)$ but also its time derivative (or equivalently the initial current density) is consistent with that of the interacting system. Once this condition is satisfied, the density of the interacting system can be reproduced from single-particle orbitals of the noninteracting system.

Since the Runge–Gross theorem also holds for the noninteracting system, fixing the initial state $|\Phi_0\rangle$ establishes a one-to-one correspondence between the density $\rho_{\mathrm{KS}}(\boldsymbol{r}, t)$ and the Kohn–Sham potential $v_{\mathrm{KS}}(\boldsymbol{r}, t)$. Therefore, if one can find $v_{\mathrm{KS}}(\boldsymbol{r}, t)$ that yields the same density as the interacting system, the interacting many-body problem can be replaced by a noninteracting problem under an effective one-body potential. This correspondence is called the Kohn–Sham mapping.

In many applications, the system at the initial time t_0 is prepared in the ground state of the one-body potential $v(\boldsymbol{r}, t_0)$. In that case, it is natural to choose the initial states of the interacting system and the Kohn–Sham system as the ground states of their respective initial Hamiltonians. Furthermore, by the Hohenberg–Kohn theorem, once the initial ground-state density is given, the corresponding initial state is also determined. Therefore, if one restricts attention to time evolution starting from a ground state, the initial-state dependence appearing in the Kohn–Sham mapping can effectively be absorbed into the initial density.

If the initial state of the Kohn–Sham system is represented by a single Slater determinant, then the time-evolved state is also represented by a single Slater determinant. In this case, the single-particle orbitals $\phi_k(\boldsymbol{r}, \sigma, t)$ forming the determinant are called Kohn–Sham orbitals, and the density is written as $\rho(\boldsymbol{r}, t) = \sum_k \sum_\sigma |\phi_k(\boldsymbol{r}, \sigma, t)|^2$. Each orbital satisfies the following time-dependent Kohn–Sham equation:

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \phi_k(\boldsymbol{r}, \sigma, t) = \left[\frac{\boldsymbol{p}^2}{2m} + v_{\mathrm{KS}}(\boldsymbol{r}, t) \right] \phi_k(\boldsymbol{r}, \sigma, t). \tag{18}$$

Thus, instead of solving the many-body time-dependent Schrödinger equation (1) directly, the practical task in TDDFT is to solve the single-particle equation given by Eq. (18).

In actual calculations, the Kohn–Sham potential is decomposed as

$$v_{\mathrm{KS}}(\boldsymbol{r}, t) = v(\boldsymbol{r}, t) + v_{\mathrm{H}}(\boldsymbol{r}, t) + v_{\mathrm{XC}}(\boldsymbol{r}, t) \tag{19}$$

Here, $v(\boldsymbol{r}, t)$ is the external one-body potential, $v_{\mathrm{H}}(\boldsymbol{r}, t)$ is the Hartree potential representing the classical mean-field interaction, and $v_{\mathrm{XC}}(\boldsymbol{r}, t)$ is the exchange-correlation potential that accounts for the remaining many-body effects not described by the Hartree term. The Hartree potential is defined by

$$v_{\mathrm{H}}(\boldsymbol{r}, t) = \int d\boldsymbol{r}'\ w(|\boldsymbol{r} - \boldsymbol{r}'|)\rho(\boldsymbol{r}', t) \tag{20}$$

On the other hand, the exchange-correlation potential is defined as

$$v_{\mathrm{XC}}(\boldsymbol{r},t) = v_{\mathrm{KS}}(\boldsymbol{r},t) - v(\boldsymbol{r},t) - v_{\mathrm{H}}(\boldsymbol{r},t) \tag{21}$$

and is chosen so that the density of the Kohn–Sham system coincides with that of the interacting system.

Up to this point, the discussion has been exact. However, explicit expressions for the exact $v_{\mathrm{KS}}(\boldsymbol{r},t)$ and $v_{\mathrm{XC}}(\boldsymbol{r},t)$ are generally not known, so in practical TDDFT calculations one must approximate $v_{\mathrm{XC}}(\boldsymbol{r},t)$ in some way. In the latter part of these notes, we use one of the most basic approximations, the adiabatic local density approximation (Adiabatic Local Density Approximation; ALDA). In this approximation, the exchange-correlation potential at each time is approximated as a function of the instantaneous electron density.

In this way, TDDFT allows the dynamics of an interacting many-body system to be treated as the time evolution of a noninteracting Kohn–Sham system that reproduces the same density. Accordingly, in what follows, the central task is to choose an appropriate approximation for the exchange-correlation potential and solve Eq. (18) numerically. In the next section, we introduce the pseudopotential method, which plays an important role in its implementation.

3 Pseudopotential Method

In the previous section, we saw that the central task in TDDFT calculations is to solve the time-dependent Kohn–Sham equation self-consistently. If one attempts to implement this directly, however, the steep behavior of the electronic wavefunctions near the nuclei gives rise to serious numerical difficulties. In this section, we introduce the **pseudopotential method**, which alleviates this difficulty while retaining, as much as possible, the essential physics of the valence electrons.

To describe an electron system driven by an external electromagnetic potential, it is natural to employ a one-body potential such as that given in Eq. (3). Calculations that explicitly treat even the electrons near the nuclei in this way are called **all-electron calculations**. However, the Coulomb potential generated by a nucleus diverges at the nuclear position, and as a result the wavefunction exhibits a sharp structure in its vicinity. For this reason, all-electron calculations are not easy to handle numerically.[2]

On the other hand, in many molecular and solid-state problems, the main role is played by the valence electrons, which are weakly bound to the nuclei, whereas the core electrons, which are deeply bound, can often be regarded as remaining almost unchanged from the ground state of the isolated atom without significant loss of accuracy. From this viewpoint, the pseudopotential method greatly reduces the computational cost by

- freezing the degrees of freedom of the core electrons, and
- replacing the valence-electron wavefunctions by functions that are smoother near the nuclei.

This is the basic idea of the pseudopotential method. In what follows, we explain the idea using the **norm-conserving pseudopotential** of Troullier–Martins [1] as an example among pseudopotentials constructed starting from atomic DFT calculations. For further details, see, for example, Ref. [2].

First, consider the radial Kohn–Sham equation for a spherically symmetric atom:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2 l(l+1)}{2m}+v_{\mathrm{KS}}^{\mathrm{AE}}[\rho^{\mathrm{AE}}(r)](r)\right]\chi_{nl}^{\mathrm{AE}}(r)=\epsilon_{nl}\chi_{nl}^{\mathrm{AE}}(r). \tag{22}$$

Here, n denotes the principal quantum number and l the orbital angular momentum quantum number. In addition, $\rho^{\mathrm{AE}}(r)$ is the density obtained in an all-electron calculation, and the Kohn–Sham potential $v_{\mathrm{KS}}^{\mathrm{AE}}[\rho^{\mathrm{AE}}(r)](r)$ can be written as the sum of the nuclear Coulomb potential, the Hartree potential $v_{\mathrm{H}}[\rho^{\mathrm{AE}}(r)](r)$, and the exchange-correlation potential $v_{\mathrm{xc}}[\rho^{\mathrm{AE}}(r)](r)$:

$$v_{\mathrm{KS}}^{\mathrm{AE}}[\rho^{\mathrm{AE}}(r)](r)=-\frac{eZ}{4\pi\epsilon_0}\frac{1}{r}+v_{\mathrm{H}}[\rho^{\mathrm{AE}}(r)](r)+v_{\mathrm{xc}}[\rho^{\mathrm{AE}}(r)](r) \tag{23}$$

Furthermore, by combining the radial wavefunction $\chi_{nl}(r)$ with the spherical harmonic $Y_{lm}(\theta,\phi)$, one obtains a Kohn–Sham orbital

$$\phi_{nlm}(\boldsymbol{r})=\frac{\chi_{nl}(r)}{r}Y_{lm}(\theta,\phi) \tag{24}$$

The first step in constructing a pseudopotential is to divide the atomic Kohn–Sham orbitals into **core electrons** and **valence electrons**. Core electrons are deeply bound and spatially localized near the nucleus, so they are assumed not to differ greatly from those of the isolated atom even in molecules and solids. By contrast, valence electrons are weakly bound and spatially extended, and they participate directly in bonding, excitation, and response to external fields; they are therefore the degrees of freedom that should be treated explicitly in actual calculations. Where one draws the boundary between core and valence is an important choice in pseudopotential

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[2] For example, if the wavefunction is expanded in plane waves, then in order to reproduce such a sharp structure one must include plane waves with very large wave numbers in the expansion, which in turn requires a very large number of basis functions.

design and must be determined appropriately according to the system and physical quantities of interest.

Even after freezing the core degrees of freedom, the all-electron wavefunction of the valence electrons remains steep near the nucleus. We therefore replace it there by a smoother function, while requiring it to coincide with the all-electron wavefunction outside a cutoff radius. Specifically, the pseudowavefunction $\chi_{nl}^{\mathrm{PP}}(r)$ is defined by

$$\chi_{nl}^{\mathrm{PP}}(r) = \begin{cases} \chi_{nl}^{\mathrm{AE}}(r) & \text{if } r > r_{c,l} \\ r^{l+1} \exp\left[p(r)\right] & \text{if } r \leq r_{c,l} \end{cases} \tag{25}$$

Here, $r_{c,l}$ is the cutoff radius, and outside this radius the pseudowavefunction coincides with the all-electron wavefunction. The function $p(r)$ is a polynomial, and in the Troullier–Martins method one uses the form

$$p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12} \tag{26}$$

The polynomial coefficients c_j are determined so as to satisfy the following seven conditions:

- Condition 1. Norm-conservation condition
  $\int_0^{r_{c,l}} dr |\chi_{nl}^{\mathrm{AE}}(r)|^2 = \int_0^{r_{c,l}} dr |\chi_{nl}^{\mathrm{PP}}(r)|^2$
- Conditions 2.–6.
  Continuity of the wavefunction and its derivatives up to fourth order at the cutoff radius $r = r_{c,l}$
- Condition 7.
  The curvature of the screened pseudopotential $v_{\mathrm{scr},l}(r)$ at the origin ($r = 0$) is zero: $v''_{\mathrm{scr},l}(r = 0) = 0$. Here, $v_{\mathrm{scr},l}(r)$ will be defined below.

In particular, a pseudopotential constructed so as to satisfy the norm-conservation condition in Condition 1 is called a **norm-conserving pseudopotential**. This means that the pseudowavefunction is designed not only to be smooth but also to preserve, as much as possible, important information contained in the all-electron wavefunction.

Next, define the electron density generated by the valence electrons represented by the pseudowavefunctions $\chi_{nl}^{\mathrm{PP}}(r)$ as

$$\rho^{\mathrm{PP}}(r) = \sum_{n,l} f_{n,l} |\chi_{nl}^{\mathrm{PP}}(r)|^2 \tag{27}$$

Here, $f_{n,l}$ is the occupation number of the state. Using this, we define the screened pseudopotential $v_{\mathrm{scr},l}(r)$ by

$$v_{\mathrm{scr},l}(r) = \begin{cases} v_{\mathrm{KS}}^{\mathrm{AE}}[\rho^{\mathrm{AE}}(r)](r) & \text{if } r > r_{c,l} \\ \epsilon_{nl} + \frac{\hbar^2}{m} \frac{l+1}{r} \frac{p'(r)}{2} + \frac{\hbar^2}{m} \frac{p''(r) + \left[p'(r)\right]^2}{2} & \text{if } r \leq r_{c,l} \end{cases} \tag{28}$$

Then the pseudowavefunction $\chi_{nl}^{\mathrm{PP}}(r)$ satisfies

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2m} + v_{\mathrm{scr},l}(r) \right] \chi_{nl}^{\mathrm{PP}}(r) = \epsilon_{nl} \chi_{nl}^{\mathrm{PP}}(r) \tag{29}$$

Therefore, once $v_{\mathrm{scr},l}(r)$ is obtained as the self-consistent field in a DFT calculation for the valence electrons, the resulting orbital functions are indeed pseudowavefunctions.

However, $v_{\mathrm{scr},l}(r)$ also contains the Hartree potential $v_{\mathrm{H}}[\rho^{\mathrm{PP}}(r)](r)$ and the exchange-correlation potential $v_{\mathrm{xc}}[\rho^{\mathrm{PP}}(r)](r)$ generated by the valence electrons. We therefore subtract them and define the pseudopotential exerted by the ion on the valence electrons as

$$v_l^{\mathrm{PP}}(r) = v_{\mathrm{scr},l}(r) - v_{\mathrm{H}}[\rho^{\mathrm{PP}}(r)](r) - v_{\mathrm{xc}}[\rho^{\mathrm{PP}}(r)](r) \tag{30}$$

Since this pseudopotential differs for each angular momentum l, it must be combined into a single operator before it can be used as an actual one-body potential. To this end, we choose one local potential $v^{\mathrm{PP}}_{\mathrm{ion,local}}(r)$ and represent the remainder as nonlocal terms:

$$\hat{v}^{\mathrm{PP}}_{\mathrm{ion}} = v^{\mathrm{PP}}_{\mathrm{ion,local}}(r) + \sum_{lm} \Delta v^{\mathrm{PP}}_{l}(r) \hat{P}_{lm} \tag{31}$$

Here, $\Delta v^{\mathrm{PP}}_{l}(r)$ appearing in the nonlocal part is defined by

$$\Delta v^{\mathrm{PP}}_{l}(r) = v^{\mathrm{PP}}_{l}(r) - v^{\mathrm{PP}}_{\mathrm{ion,local}}(r) \tag{32}$$

In addition, $\hat{P}_{lm}$ is the angular-momentum projection operator, defined for an arbitrary function $f(\boldsymbol{r})$ by

$$\hat{P}_{lm} f(\boldsymbol{r}) = Y_{lm}(\theta,\phi) \int d\Omega \; Y^{*}_{lm}(\theta,\phi) f(\boldsymbol{r}) \tag{33}$$

If the pseudopotential in Eq. (31) is used as the one-body potential in the Kohn–Sham equation, then, by construction, the pseudowavefunction $\chi^{\mathrm{PP}}_{nl}(r)$ is a self-consistent solution. The local potential $v^{\mathrm{PP}}_{\mathrm{ion,local}}(r)$ may in principle be chosen freely, but in many cases one adopts the pseudopotential $v^{\mathrm{PP}}_{l}(r)$ corresponding to a particular angular momentum l. If the angular momentum used as the reference for the local potential is denoted by l_{ref}, then the nonlocal potential $\Delta v^{\mathrm{PP}}_{l}(r)$ vanishes for $r > \max(r_{c,l}, r_{c,l_{\mathrm{ref}}})$ and thus acts only within a finite spatial range.

Equation (31) realizes both the freezing of the core degrees of freedom and the introduction of smooth pseudowavefunctions, but in actual numerical calculations it is computationally disadvantageous to treat the angular-momentum projection operators directly. Therefore, in many practical calculations one uses the Kleinman–Bylander separable form and writes the pseudopotential as

$$\hat{v}^{\mathrm{PP,KB}}_{\mathrm{ion}} = v^{\mathrm{PP}}_{\mathrm{ion,local}}(r) + \sum_{lm} \frac{|\Delta v^{\mathrm{PP}}_{l}(r)\phi^{\mathrm{PP}}_{lm}\rangle\langle\phi^{\mathrm{PP}}_{lm}\Delta v^{\mathrm{PP}}_{l}(r)|}{\langle\phi^{\mathrm{PP}}_{lm}|\Delta v^{\mathrm{PP}}_{l}(r)|\phi^{\mathrm{PP}}_{lm}\rangle} \tag{34}$$

Here, the state vectors $|\phi^{\mathrm{PP}}_{lm}\rangle$ and $|\Delta v^{\mathrm{PP}}_{l}(r)\phi^{\mathrm{PP}}_{lm}\rangle$ are introduced by

$$\langle\boldsymbol{r}|\phi^{\mathrm{PP}}_{lm}\rangle = \frac{\chi^{\mathrm{PP}}_{nl}(r)}{r} Y_{lm}(\theta,\phi), \tag{35}$$

$$\langle\boldsymbol{r}|\Delta v^{\mathrm{PP}}_{l}(r)\phi^{\mathrm{PP}}_{lm}\rangle = \Delta v^{\mathrm{PP}}_{l}(r) \frac{\chi^{\mathrm{PP}}_{nl}(r)}{r} Y_{lm}(\theta,\phi) \tag{36}$$

In the form of Eq. (34), the nonlocal term can be evaluated more efficiently.

In this way, the pseudopotential method freezes the core electrons and introduces smooth pseudowavefunctions and an effective one-body potential for the valence electrons, thereby greatly reducing the computational cost while preserving the essential content of all-electron calculations. In the following sections, we use pseudopotentials constructed in this manner to discuss concretely real-time electron dynamics calculations for molecules and solids.

4 Real-Time Electron Dynamics Calculations for Molecules

In this section, we discuss electron dynamics calculations for isolated systems under isolated boundary conditions, taking molecules as examples. For simplicity, spin degeneracy is assumed.

4.1 Ground-State Calculations for Molecules

In real-time electron dynamics calculations for isolated systems, one must first obtain the ground state of the molecule in the absence of external fields before starting the time evolution. This provides the initial condition for the Kohn–Sham orbitals that are propagated in time according to Eq. (18).

In this subsection, we use an isolated N_2 molecule as an example and explain the basic idea of ground-state calculations for molecules, together with points to check in the input files. For simplicity, spin degeneracy is assumed, so that each spatial orbital is occupied by two electrons.

The ground state without external fields is obtained by solving the time-independent Kohn–Sham equation

$$\left[\frac{\boldsymbol{p}^2}{2m} + \hat{v}_{\text{ion}} + v_{\text{H}}\left[\rho\right](\boldsymbol{r}) + v_{\text{xc}}\left[\rho\right](\boldsymbol{r})\right]\phi_n(\boldsymbol{r}) = \epsilon_n\phi_n(\boldsymbol{r}) \tag{37}$$

self-consistently. Here, $\phi_n(\boldsymbol{r})$ is a Kohn–Sham orbital, ϵ_n is its energy eigenvalue, and $\rho(\boldsymbol{r})$ is the electron density. The operator $\hat{v}_{\text{ion}}$ is the pseudopotential representing the interaction between the electrons and the ions, $v_{\text{H}}\left[\rho\right](\boldsymbol{r})$ is the Hartree potential, and $v_{\text{xc}}\left[\rho\right](\boldsymbol{r})$ is the exchange-correlation potential. The basic idea of pseudopotentials was described in the previous section; in practical calculations, core electrons are not treated explicitly, and $\hat{v}_{\text{ion}}$ is used as an effective potential acting on the valence electrons.

Assuming spin degeneracy, the electron density is constructed from the occupied Kohn–Sham orbitals as

$$\rho(\boldsymbol{r}) = 2\sum_{n=1}^{N_{\text{occ}}} \left|\phi_n(\boldsymbol{r})\right|^2 \tag{38}$$

Here, N_{occ} is the number of occupied spatial orbitals, and the factor of 2 at the beginning of the right-hand side represents spin degeneracy. Therefore, if the number of electrons treated explicitly is denoted by N_e, the relation

$$N_e = \int d\boldsymbol{r}\ \rho(\boldsymbol{r}) = 2N_{\text{occ}} \tag{39}$$

must be satisfied. When pseudopotentials are used, it should be noted that N_e here is not the total number of electrons, but is determined by the number of valence electrons explicitly treated by the pseudopotential.

Equation (37) has the form of an ordinary eigenvalue problem. However, since $v_{\text{H}}\left[\rho\right]$ and $v_{\text{xc}}\left[\rho\right]$ depend on the unknown density $\rho(\boldsymbol{r})$, the calculation is not completed by diagonalizing the Hamiltonian only once. In practice, the following procedure is iterated.

1. Assume an initial density $\rho^{(0)}(\boldsymbol{r})$.
2. Construct the Kohn–Sham Hamiltonian $\hat{h}_{\text{KS}}[\rho^{(i)}]$ from that density.
3. Solve the eigenvalue problem and obtain the orbitals $\phi_n^{(i)}(\boldsymbol{r})$.
4. Construct a new density $\rho^{(i+1)}(\boldsymbol{r})$ using Eq. (38).
5. Repeat the procedure until the density, eigenvalues, or total energy no longer change appreciably.

When this iterative calculation converges, the resulting density and effective potential are mutually consistent, and the solution is regarded as a self-consistent ground-state solution.

Source code 3 shows an example input file for a ground-state calculation of an N_2 molecule using Octopus. In this example, a ground-state calculation is specified as the calculation mode, and the isolated molecule is treated on a real-space grid. When reading the input file, it is useful to pay particular attention to the following points.

- `CalculationMode = gs` specifies that a ground-state calculation is to be performed.
- `FromScratch = yes` specifies that the calculation should be started anew without reusing data generated in previous calculations.
- `Coordinates` specifies the atomic species and atomic positions that make up the molecule. If one wants to change the molecular geometry, such as the bond length, this part should be adjusted following the existing examples in the lecture notes.
- `Radius` controls the size of the computational region containing the isolated molecule, while `Spacing` controls the spacing of the real-space grid. If the molecule is too close to the boundary of the computational region, the tail of the density is artificially truncated; convergence should therefore be checked later.
- `XCFunctional` specifies the exchange-correlation functional. Using the same approximation as in the subsequent time-dependent calculation ensures theoretical consistency between the ground state and the time evolution.
- `PseudopotentialSet` specifies the set of pseudopotentials to be used.
- `Eigensolver`, `MaximumIter`, and `EigensolverTolerance` are related to the method for solving the eigenvalue problem and to the convergence conditions. If the calculation does not converge, the number of iterations and the tolerance should be reconsidered.

`https://shunsuke-sato.github.io/page/etc/lecture_notes/src_tddft_note/lin_res_n2/inp_gs`

Source Code 1: Octopus input file: ground state of an N_2 molecule

```
CalculationMode = gs
FromScratch = yes

Radius = 10.0

XCFunctional = lda_x + lda_c_pw
Spacing = 0.4

ExtraStates = 2

PseudopotentialSet = hgh_lda

# User defined valiable, (N-N distance)
NN_distance = 2.0

%Coordinates
 "N" |  0 |  0 |  0.5*NN_distance
 "N" |  0 |  0 | -0.5*NN_distance
%

Eigensolver = cg
MaximumIter = 60
ConvEigenError = yes
EigensolverTolerance = 1e-8
```

Source code 2 is an example shell script for running the ground-state calculation. In this example, the input file for the ground-state calculation is copied to the standard input-file name read by Octopus, and the standard output during execution is saved to a log file. The path to the Octopus executable, the number of MPI processes, and the number of OpenMP threads depend on the computational environment, so these should be changed according to each user's own environment.

`https://shunsuke-sato.github.io/page/etc/lecture_notes/src_tddft_note/lin_res_n2/run_gs.sh`

Source Code 2: Shell script for running the ground-state calculation of an N_2 molecule

```bash
#!/bin/bash

export OMP_NUM_THREADS=2
export MY_OCTOPUS="/work/sato/octopus_tutorial/octopus_execute/install/bin/octopus"


cp inp_gs inp

mpirun -np 1  "${MY_OCTOPUS}" >log.gs.log 2>&1
```

After the calculation has finished, check the output log file. If the grid spacing is too coarse, the accuracy of the ground-state energy and eigenvalues deteriorates. Therefore, in actual research calculations, it is necessary to vary `Radius` and `Spacing` and confirm that the ground-state energy and important eigenvalues change only negligibly.

The ground-state Kohn–Sham orbitals and density obtained in this way serve as the initial state for the linear-response calculation discussed in the next subsection. Therefore, before proceeding to the time-dependent calculation, it is important to confirm that the ground state obtained here is physically and numerically reasonable.

4.2 Linear-Response Calculations for Molecules

Next, to investigate the optical response of a molecule, we analyze the electron dynamics driven by an optical electric field. Since the wavelength of light, on the order of micrometers, is much larger than the spatial scale of electron motion, on the order of nanometers, the optical electric field can be regarded as spatially uniform within the region where the electron dynamics takes place. This approximation is called the **long-wavelength approximation** or the **dipole approximation**.

The dynamics of electrons moving under a spatially uniform external electric field $\boldsymbol{E}(t)$ is described by the following time-dependent Kohn–Sham equation:

$$i\hbar\frac{\partial}{\partial t}\psi_m(\boldsymbol{r},t) = \left[\frac{\boldsymbol{p}^2}{2m} + \hat{v}_{\mathrm{ion}} + v_{\mathrm{H}}\left[\rho(\boldsymbol{r},t)\right](\boldsymbol{r},t) + v_{\mathrm{xc}}\left[\rho(\boldsymbol{r},t)\right](\boldsymbol{r},t) - e\boldsymbol{E}(t)\cdot\boldsymbol{r}\right]\psi_m(\boldsymbol{r},t) \tag{40}$$

Here, $\rho(\boldsymbol{r},t)$ is the time-dependent electron density, which is constructed from the time-dependent Kohn–Sham orbitals $\psi_m(\boldsymbol{r},t)$ as

$$\rho(\boldsymbol{r},t) = 2\sum_{m=\mathrm{occ}}|\psi_m(\boldsymbol{r},t)|. \tag{41}$$

The Hartree potential $v_{\mathrm{H}}\left[\rho(\boldsymbol{r},t)\right](\boldsymbol{r},t)$ and the exchange-correlation potential $v_{\mathrm{xc}}\left[\rho(\boldsymbol{r},t)\right](\boldsymbol{r},t)$ are functionals of $\rho(\boldsymbol{r},t)$. In general, the exchange-correlation potential at time t depends on the density $\rho(\boldsymbol{r},t')$ at all earlier times ($t' \leq t$); this dependence is called a memory effect. In practice, one almost always employs an **adiabatic approximation**, in which the exchange-correlation potential $v_{\mathrm{xc}}\left[\rho(\boldsymbol{r},t)\right](\boldsymbol{r},t)$ is approximated using only the density $\rho(\boldsymbol{r},t)$ at the same time t.

Let us now consider the electric dipole moment $\boldsymbol{d}(t)$ induced in the system by the external electric field $\boldsymbol{E}(t)$. If an electric field $\boldsymbol{E}(t)$ is applied to a system that was in its ground state at time t_0, the induced electric dipole moment can be written in terms of the electron density $\rho(\boldsymbol{r},t)$ as

$$\boldsymbol{d}(t) = -e\int d\boldsymbol{r}\ \boldsymbol{r}\left[\rho(\boldsymbol{r},t) - \rho(\boldsymbol{r},t_0)\right]. \tag{42}$$

Once the electric field $\boldsymbol{E}(t)$ is given, $d_a(t)$ is determined by solving the time-dependent Kohn–Sham equation [Eq. 40]. Thus, the electric dipole moment $\boldsymbol{d}(t)$ induced by the field is a functional of the electric field $\boldsymbol{E}(t)$. If the electric field $\boldsymbol{E}(t)$ is sufficiently weak, the electric dipole moment can be approximated by an expansion up to first order in the electric field:

$$d_a(t) = \sum_{b=\{x,y,z\}} \int_{-\infty}^{\infty} dt' \ \alpha_{ab}(t,t')E_b(t'). \tag{43}$$

Here, $d_a(t)$ and $E_b(t)$ are the a component of $\boldsymbol{d}(t)$ and the b component of $\boldsymbol{E}(t)$, respectively. The quantity $\alpha_{ab}(t,t')$ is a response tensor that relates the external field to the response. If the system has time-translation symmetry, the response tensor depends only on the time difference $t - t'$ and can be written as

$$d_a(t) = \sum_{b=\{x,y,z\}} \int_{-\infty}^{\infty} dt' \ \alpha_{ab}(t-t')E_b(t'). \tag{44}$$

Taking the Fourier transform of both sides gives the following relation:

$$\tilde{d}_{a(\omega)} = \sum_{b=\{x,y,z\}} \tilde{\alpha}_{ab}(\omega)\tilde{E}_b(\omega). \tag{45}$$

Here, the Fourier transforms are defined as

$$\tilde{d}_{a(\omega)} = \int_{-\infty}^{\infty} dt \ d_a(t)e^{i\omega t} \tag{46}$$

$$\tilde{\alpha}_{ab}(\omega) = \int_{-\infty}^{\infty} dt \ \alpha_{ab}(t)e^{i\omega t} \tag{47}$$

$$\tilde{E}_b(\omega) = \int_{-\infty}^{\infty} dt \ E_b(t)e^{i\omega t}. \tag{48}$$

In particular, $\tilde{\alpha}_{ab}(\omega)$ is called the polarizability tensor.

Let us now examine an important property of the polarizability tensor $\tilde{\alpha}_{ab}(\omega)$. The electric dipole moment in Eq. (44) is driven by the electric field $E(t)$, but causality requires that an electric field at a future time cannot affect the electric dipole moment at the present time. That is, for $\boldsymbol{d}(t)$ at time t, the electric field $\boldsymbol{E}(t')$ at a future time ($t' > t$) has no influence. This is guaranteed by the fact that the polarizability tensor in the time domain, $\alpha_{ab}(t)$, vanishes for $t < 0$. Therefore, the following equality holds:

$$\alpha_{ab}(t) = \Theta(t)\alpha_{ab}(t). \tag{49}$$

Here, $\Theta(t)$ is the Heaviside step function. Fourier transforming both sides yields

$$\tilde{\alpha}_{ab}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \ \tilde{\Theta}(\omega - \omega')\tilde{\alpha}_{ab}(\omega'). \tag{50}$$

Here, $\tilde{\Theta}(\omega)$ is the Fourier transform of $\Theta(t)$ and is given by

$$\tilde{\Theta}(\omega) = \pi\delta(\omega) + i\mathcal{P}\frac{1}{\omega}. \tag{51}$$

Here, $\mathcal{P}$ denotes the Cauchy principal value. Using this expression, Eq. (50) can be rewritten as

$$\begin{aligned}\tilde{\alpha}_{ab}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \ \left[\pi\delta(\omega - \omega') + i\mathcal{P}\frac{1}{\omega - \omega'}\right]\tilde{\alpha}_{ab}(\omega') \\ &= \frac{1}{2}\tilde{\alpha}_{ab}(\omega) + \frac{i}{2\pi}\mathcal{P}\int_{-\infty}^{\infty} d\omega' \ \frac{\alpha_{ab}(\omega')}{\omega - \omega'}. \end{aligned} \tag{52}$$

Therefore, we obtain

$$\tilde{\alpha}_{ab}(\omega) = \frac{i}{\pi}\mathcal{P}\int_{-\infty}^{\infty} d\omega' \ \frac{\alpha_{ab}(\omega')}{\omega - \omega'} \tag{53}$$

By considering the real and imaginary parts of both sides, one obtains the following **Kramers–Kronig relations**:

$$\mathrm{Re}\left[\tilde{\alpha}_{ab}(\omega)\right] = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} d\omega' \ \frac{\mathrm{Im}\left[\alpha_{ab}(\omega')\right]}{\omega' - \omega} \tag{54}$$

$$\mathrm{Im}\left[\tilde{\alpha}_{ab}(\omega)\right] = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} d\omega' \ \frac{\mathrm{Re}\left[\alpha_{ab}(\omega')\right]}{\omega' - \omega}. \tag{55}$$

Thus, as a consequence of causality, the real and imaginary parts of the Fourier transform of a response function are related to each other.

Next, we discuss how to evaluate the polarizability tensor $\tilde{\alpha}_{ab}(\omega)$ in practice. The relation between the polarization and the electric field in Eq. (45) holds for an arbitrary electric field $\boldsymbol{E}(t)$, provided that the field is sufficiently weak.

`https://shunsuke-sato.github.io/page/etc/lecture_notes/src_tddft_note/lin_res_n2/inp_td`

Source Code 3: Octopus input file: linear response of an N_2 molecule

```
CalculationMode = td
FromScratch = yes

Radius = 10.0

XCFunctional = lda_x + lda_c_pw
Spacing = 0.4

ExtraStates = 0

PseudopotentialSet = hgh_lda

# User defined valiable, (N-N distance)
NN_distance = 2.0

%Coordinates
 "N" |  0 |  0 |  0.5*NN_distance
 "N" |  0 |  0 | -0.5*NN_distance
%

Eigensolver = cg
MaximumIter = 60
ConvEigenError = yes
EigensolverTolerance = 1e-8


TDPropagator = aetrs
TDExponentialMethod = taylor
TDExpOrder = 4
TDPropagationTime = 10*fs
TDTimeStep = 0.08

TDDeltaStrength = 0.01
TDPolarizationDirection = 3
```

`https://shunsuke-sato.github.io/page/etc/lecture_notes/src_tddft_note/lin_res_n2/run_td.sh`

Source Code 4: Shell script for running the linear-response calculation of an N_2 molecule

```
#!/bin/bash

export OMP_NUM_THREADS=4
export MY_OCTOPUS="/work/sato/octopus_tutorial/octopus_execute/install/bin/octopus"

```

```
cp inp_td inp

mpirun -np 2 "${MY_OCTOPUS}" >log.td.log 2>&1
```

5 Real-Time Electron Dynamics Calculations for Solids

References

[1] N. Troullier and J. L. Martins, ”Efficient pseudopotentials for plane-wave calculations”, Phys. Rev. B 43, 1993 (1991).

[2] M. Oliveira and F. Nogueira, ”Generating relativistic pseudo-potentials with explicit incorporation of semi-core states using APE, the Atomic Pseudo-potentials Engine”, Comput. Phys. Comm. 178, 524 (2008).