Time-dependent density functional theory and molecular properties

Stan van Gisbergen
Vrije Universiteit Amsterdam

Contents

I. GENERAL INTRODUCTION

A. Outline of this work

The aim of this write-up is to provide some background information about the theory underlying analytic molecular property calculations in both ground-state and time-dependent DFT. Some results from perturbation theory and response theory are presented. Furthermore this work tries to give some insight into the strengths and weaknesses of the TDDFT approach to excited states and place it in the framework of other theoretical methods to obtain excited state properties. In the lectures, some illustrative examples are given to explain what TDDFT is typically used for.

B. Introduction: The place of DFT within correlated methods to electronic structure

In comparison to other correlated methods to electronic structure theory, like Configuration Interaction (CI), Coupled Cluster (CC), Möller-Plesset Perturbation Theory, Density functional Theory (DFT) takes a somewhat special place. Its aim is not to obtain a good approximation to the ground state wave-function of the system, but rather to find the energy of the system as a functional of the density, without reference to the wavefunction. That such an approach is possible and is indeed formally justified was shown by Hohenberg and Kohn in 1964 [1]. Their proof that all observables of a many electron system, including the energy, are unique functionals of the electron density provides the theoretical basis for DFT. This Hohenberg-Kohn theorem does not yet provide a practical approach for calculations. For that the Kohn–Sham equations are needed. In their 1965 paper Kohn and Sham [2] showed that if, for a non-interacting particle system, a *local* external potential exists (called the Kohn–Sham potential), such that the density of the noninteracting particle system is identical to the density of the interacting particle system, then this local potential must be unique.

This provides a simple practical scheme for a system of non-interacting particles in a local potential, which may in principle provide exact results for the ground-state. However, the local potential is unknown and needs to be approximated. In practice the quality of DFT results therefore depend on the reliability for the exchange-correlation (xc) potential and energy functionals.

This DFT scheme has become very popular for applications in quantum chemistry for various reasons. First of all, reliable xc functionals have been developed which enables one the obtain accurate numbers for many types of properties, such as geometries, bonding energies, vibrational frequencies, etc. Second, the efficiency of the DFT approach allows one to treat large molecules (100 atoms or more) which occur in practical chemical problems. In this respect DFT compares favorably to more expensive methods like MRCI and CC, although these are preferable from a fundamental viewpoint. DFT is therefore a powerful, quantitative predictive tool in theoretical chemistry.

Ordinary ground-state DFT is restricted however to the treatment of ground-state properties. Properties related to excited states or to external fields which are time-dependent (such as the electric field from a laser beam) could not be treated with DFT. Because of the usefulness of DFT for ground-state properties people have been looking at ways to apply DFT to such problems as well. At the current point in time one can safely say that time-dependent DFT (TDDFT) is the most successful and theoretically most elegant way to treat excited states within a density functional context.

By now, TDDFT methods have been applied by many groups to various molecular properties. It has become clear that the advantages and disadvantages of TDDFT are similar to those of ground-state DFT. In particular, it allows one to obtain reliable excited state properties for fairly large molecules.

C. Useful references

A few references are given which may be useful for further study. Many text books are available on ground-state density functional theory. The ones by Dreizler and Gross [3] and Parr and Yang [4] are classics. The Dreizler–Gross book is more formal, the Parr-Yang book is more "chemical". Good sections on perturbation and response theory are to be found in Refs. [5,6]. Several reviews on time-dependent density functional theory are available by Gross and co-workers [7–9]. A paper by Casida [10] gives a nice overview of TDDFT through the eyes of a quantum chemist. It makes direct connections to the time-dependent Hartree–Fock approach and introduces the eigenvalue equation which is generally used for calculating excitation energies within TDDFT. The Bauernschmitt–Ahlrichs paper is also quite clear [11]. The TDDFT approach in the Amsterdam Density Functional program (ADF) is described in Refs. [12,13]. References to the practical examples discussed in the lectures are available at http://tc.chem.vu.nl/∼vgisberg/abstracts.html. Some applications of TDDFT to periodic structures are available at http://theochem.chem.rug.nl/publications/index.html.

II. DENSITY FUNCTIONAL THEORY, HOHENBERG–KOHN THEOREM AND KOHN–SHAM EQUATIONS

A. The Hohenberg–Kohn theorem

Is it possible to take the electron density as the basic variable for a many-electron problem instead of the full wavefunction? If that is true it would, at first sight, imply a drastic reduction in the complexity of the problem, as one considers a quantity which depends on only 3 spatial coordinates, instead of the wavefunction which depends on the coordinates of all electrons.

The Hohenberg-Kohn theorem tells us that the system is indeed fully specified by the electron density. In order to understand why this is not so strange as it looks, we repeat a famous (unpublished) argument by Bright Wilson. He explains that the electron density determines the number of electrons in the system in a trivial manner (integrate the density over all space). Furthermore the density determines the nuclear positions (the location of the cusps in the density). The atomic numbers of the nuclei are determined by the slope of the density at the nuclei. But if we know the position and atomic numbers of all nuclei and the number of electrons in the system, we can write down the Schrödinger equation, solve it (in principle) and calculate all properties of the system that we are interested in.

Although this argument is very clever and shows that the basic idea in DFT is not really absurd, it is not obvious how this argument should be extended to the case where external fields may be present. We therefore consider the original Hohenberg–Kohn theorem below, in order to *prove* that the electron density can indeed be taken as the basic variable.

The following arguments were taken from Refs. [3,4]. Consider an N-electron molecular system in the Born–Oppenheimer nonrelativistic approximation. The Hamiltonian $\hat{H}$ in the Schrödinger Equation (SE)

$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots) \tag{1}$$

consists of the kinetic energy $\hat{T}$, the nuclear-electron interaction $\hat{V}_{ne}$, and the electron-electron interaction $\hat{V}_{ee}$:

$$\hat{H} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} \tag{2}$$

$$\hat{T} = \sum_{i=1}^{N}(-\nabla_i^2) \tag{3}$$

$$\hat{V}_{ne} = \sum_{i=1}^{N} v(\mathbf{r}_i) = -\sum_{i=1}^{N}\sum_{\alpha}\frac{Z_\alpha}{r_{i\alpha}} \tag{4}$$

$$\hat{V}_{ee} = \sum_{i<j}^{N}\frac{1}{r_{ij}} \tag{5}$$

$$\tag{6}$$

The lowest energy of the system, E_0, can be found from the Rayleigh–Ritz minimization principle:

$$E_0 = \min_{\Psi}\frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{7}$$

Wave function based methods attempt to search a suitable part of the space of trial functions. (For example, in Hartree-Fock theory the best single Slater determinant is sought.) In order to replace this with a search over densities, the Hohenberg–Kohn (HK) theorem aims to establish a one-to-one mapping between the electron density ρ:

$$\rho(\mathbf{x}_1) = \int \mid \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \mid^2 d\mathbf{x}_2 \ldots d\mathbf{x}_N \tag{8}$$

and the external potential $\hat{V}_{ne}$. The part of the mapping

$$\hat{V}_{ne} \longrightarrow \Psi \longrightarrow \rho \tag{9}$$

is rather straight-forward. With each $\hat{V}_{ne}$ we can connect a corresponding wavefunction Ψ by solving the SE. Then we can find the corresponding density by integrating the square of the wavefunction (Eq. 8).

In order to show that ρ determines $\hat{V}_{ne}$ (that the arrows point in two directions), we have to prove two things: i) if Ψ and Ψ' are different, they cannot lead to the same density. ii) if $\hat{V}_{ne}$ and $\hat{V}'_{ne}$ are different (by more than a constant) they will not lead to the same wavefunction.

For a *nondegenerate* ground state, this goes as follows: Starting with ii), one has:

$$(\hat{T} + \hat{V}_{ee} + \hat{V}_{ne})|\Psi\rangle = E_{\rm gs}|\Psi\rangle \tag{10}$$

$$(\hat{T} + \hat{V}_{ee} + \hat{V}'_{ne})|\Psi'\rangle = E'_{\rm gs}|\Psi'\rangle \tag{11}$$

If $\Psi = \Psi'$ we get

$$(\hat{V}_{ne} - \hat{V}'_{ne})|\Psi\rangle = (E_{\rm gs} - E'_{\rm gs})|\Psi\rangle \tag{12}$$

In other words, if the external potentials differ by more than a constant, the wavefunctions are not identical, which is what we were trying to prove.

In the case of i) one proves that $\Psi \neq \Psi'$ implies $\rho(r) \neq \rho'(r)$.

$$E_{gs} = \langle\Psi|\hat{H}|\Psi\rangle < \langle\Psi'|\hat{H}|\Psi'\rangle \tag{13}$$

(Here the strict <-sign holds only because of the demanded nondegeneracy of the ground state)

$$\langle\Psi'|\hat{H}|\Psi'\rangle = \langle\Psi'|\hat{H}' + \hat{V}_{ne} - \hat{V}'_{ne}|\Psi'\rangle = E'_{gs} + \int d\mathbf{r}\rho'(\mathbf{r})[V_{ne}(r) - V'_{ne}(r)] \tag{14}$$

Similarly we have

$$E'_{gs} < E_{gs} + \int d\mathbf{r}\rho(\mathbf{r})[V'_{ne}(r) - V_{ne}(r)] \tag{15}$$

Together this leads to the contradiction

$$E_{gs} + E'_{gs} < E_{gs} + E'_{gs} \tag{16}$$

These two proofs show that the maps between $\hat{V}_{ne}$, Ψ, and ρ, are bijective (one-to-one).

$$\hat{V}_{ne} \longleftrightarrow \Psi \longleftrightarrow \rho \tag{17}$$

As a consequence of the bijective map $\Psi \longleftrightarrow \rho$, every observable $\hat{O}$ of the system is a unique functional of the density:

$$\langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle = \hat{O}[\rho] \tag{18}$$

The map $\rho \longrightarrow \hat{V}_{ne}$ tells us that ρ determines the external potential and thus the entire Hamiltonian. Additionally, the HK theorem tells us that for the energy functional of a system in a particular external potential v_0

$$E_{v_0}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{V}_{ee} + \hat{V}_{ne,0} | \Psi[\rho] \rangle, \tag{19}$$

the exact ground state density can be found by minimization of $E_{v_0}[\rho]$:

$$E_0 = \min_{\rho} E_{v_0}[\rho] \tag{20}$$

The part of the energy functional, $F_{\mathrm{HK}}[\rho]$, which does not involve the external potential is a *universal* density functional:

$$E_{v_0[\rho]} = F_{HK}[\rho] + \int d\mathbf{r} v_0(\mathbf{r}) \rho(\mathbf{r}) \tag{21}$$

$$F_{HK}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{V}_{ee} | \Psi[\rho] \rangle \tag{22}$$

It is the same for atoms, molecules or solids. Usually $\hat{V}_{ee}$ is the Coulomb potential, but it can be anything in principle.

All this does not yet provide a practical scheme to get good approximations to the ground-state density or to the energy, because it does not tell us what F_{HK} is or how to perform the map $\rho \to \Psi$ in practice. For that one needs to go a step further: to the Kohn–Sham equations.

B. The Kohn–Sham equations

Kohn and Sham [2] considered a system of non-interacting (i.e. $\hat{V}_{ee} = 0$) electrons moving in an external potential $\hat{V}_{s,0}$. The SE for this system reads:

$$\left(-\frac{\nabla^2}{2} + v_{s,0}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \tag{23}$$

The density of this system is determined by the N lowest energy orbitals

$$\rho_s(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2. \tag{24}$$

The kinetic energy of this noninteracting electron system is given by:

$$T_s[\rho] = \sum_{i=1}^{N} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle \tag{25}$$

The central assumption in the Kohn–Sham (KS) scheme is that, for each interacting electron system with external potential v_0, a local potential $v_{s,0}(\mathbf{r})$ exists (nowadays called the Kohn–Sham potential) such that the density of the noninteracting system equals the density of the interacting system. The HK theorem then tells us that this potential must be unique.

In order to find a useful expression for the Kohn–Sham (KS) potential, we rewrite the total energy of the system as:

$$E[\rho] = T_s[\rho] + \int d\mathbf{r} v_0(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{xc}}[\rho] \tag{26}$$

where the xc energy functional $E_{\mathrm{xc}}[\rho]$ has been introduced:

$$E_{\mathrm{xc}}[\rho] = F_{\mathrm{HK}}[\rho] - T_s[\rho] - \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{27}$$

According to the HK theorem, the energy functional should be stable against small variations $\delta\rho(\mathbf{r})$ around the exact density $\rho_0(\mathbf{r})$:

$$\delta E[\rho] \mid_{\rho=\rho_0} = 0 \tag{28}$$

However, we can also look at variations with respect to orbital changes, provided we apply certain constraints to the non-interacting orbitals, such as orthonormality:

$$\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij} \tag{29}$$

which keeps the density normalized and the expression for the kinetic energy formula valid. Introducing these constraints in the form of Lagrangian multipliers ε_{ij}, we get:

$$\Omega[\{\phi_i\}] = E[\rho] - \sum_i\sum_j \varepsilon_{ij}\int d\mathbf{r}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) \tag{30}$$

$$\delta\Omega[\{\phi_i\}] = 0 \tag{31}$$

This leads to the KS equations (after a unitary transformation which makes the ε-matrix diagonal)

$$[-\frac{\nabla^2}{2} + v_0(\mathbf{r}) + \int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\partial E_{\mathrm{xc}}}{\partial\rho(\mathbf{r})}]\phi_i = \varepsilon_i\phi_i(\mathbf{r}) \tag{32}$$

In other words, the Kohn–Sham potential is given by:

$$v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + \int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\mathrm{xc}}(\mathbf{r}), \tag{33}$$

where

$$v_{\mathrm{xc}}(\mathbf{r}) = \frac{\partial E_{\mathrm{xc}}}{\partial\rho(\mathbf{r})} \tag{34}$$

is the xc potential.

As the KS potential depends on the density, the equations have to be solved self-consistently, i.e., from an initial guess for the orbitals one calculates the KS potential, which can be used in the next iteration to get a new set of orbitals and the density. This continues until no more changes occur.

What has been achieved by setting up the Kohn–Sham equations? One aspect is that it provides a direct route to calculate the density, and from that the energy of the system, once an approximation for $E_{\rm xc}$ is made. Another advantage is that the kinetic energy of the noninteracting system can be calculated exactly from the orbitals. Instead of finding a good density functional for the full kinetic energy $T[\rho]$, one only has to find a good approximation for $T[\rho] - T_s[\rho]$. In other words, the xc part of the energy should be a relatively small part of the total.

C. The time-dependent Kohn–Sham equations

If we want to arrive at a set of time-dependent Kohn–Sham equations, several differences with respect to the static case arise, which severely complicate the derivations. For that reason, we shall not attempt to be rigorous in this section, but merely point out a few important differences with respect to the static case and merely sketch how one arrives at the time-dependent Kohn–Sham equations.

Starting from the TD SE [8],

$$i\frac{\partial}{\partial t}\Psi(t) = \hat{H}(t)\Psi(t), \tag{35}$$

where the external potential can now be time-dependent:

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}(t) \tag{36}$$

we shall consider densities evolving from a fixed initial many-particle state $\Psi(t_0) = \Psi_0$. (This is the first difference with respect to the static case, where there is no such initial state dependence). For each initial state Ψ_0, the TD SE defines a map

$$v(\mathbf{r},t) \longrightarrow \Psi(t) \tag{37}$$

and from the wavefunction we can get the density:

$$\Psi(t) \longrightarrow \rho(\mathbf{r},t) = \langle\Psi(t)|\hat{\rho}(\mathbf{r})|\Psi(t)\rangle \tag{38}$$

Together this defines a map $v \longrightarrow \rho$. A time-dependent analogue of the HK theorem requires the proof that this map is invertible, in this case up to a purely time-dependent function $c(t)$ [in the ground state case this was an arbitrary constant].

A rough sketch of the proof goes as follows: Assume that the external potentials can be expanded in a Taylor series around $t = t_0$. Show that, if two external potentials v and v' differ by more than a purely time-dependent function $c(t)$, the corresponding current densities j and j' will be different. Then use the continuity equation

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = -\nabla\cdot\mathbf{j}(\mathbf{r},t) \tag{39}$$

to show that the densities ρ and ρ' must also differ. For the full proof, see Refs. [14,8].

From this we can conclude that the many-particle wave function is a functional of the density up to a purely time-dependent phase factor:

$$\Psi(t) = e^{-i\alpha(t)}\Phi[\rho](t) \tag{40}$$

The expectation value of any operator $\hat{O}$ is consequently a *unique* functional of the density because the phase factor drops out of the equation:

$$O[\rho](t) = \langle\Phi[\rho](t)|\hat{O}(t)|\Phi[\rho](t)\rangle \tag{41}$$

This was the equivalent of the HK theorem for the static case. Now we want to move on and write down the time-dependent KS equations. Again we know that the local potential Kohn–Sham potential $v_s(\mathbf{r},t)$ of a noninteracting density system which yields the exact time-dependent density $\rho(\mathbf{r},t)$ is unique if it exists. We again have to assume that such a potential indeed exists.

Under that assumption, the density of the interacting particle system $\rho(\mathbf{r},t)$ is equal to the density of the noninteracting particle system $\rho_s(\mathbf{r},t)$, which is the sum of the squares of the time-dependent Kohn–Sham orbitals:

$$\rho(\mathbf{r},t) = \rho_s(\mathbf{r},t) = \sum_{i=1}^{N}|\phi_i(\mathbf{r},t)|^2 \tag{42}$$

where the time-dependent KS orbitals are again obtained from the noninteracting particle equations:

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t) = \left(-\frac{\nabla^2}{2} + v_s[\rho](\mathbf{r},t)\right)\phi_j(\mathbf{r},t), \tag{43}$$

where the single-particle potential is written as

$$v_s[\rho](\mathbf{r},t) = v(\mathbf{r},t) + \int d\mathbf{r}'\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\mathrm{xc}}(\mathbf{r},t). \tag{44}$$

Here $v(\mathbf{r},t)$ is the time-dependent external field, $\int d\mathbf{r}'\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}$ is the time-dependent Hartree potential, and the remainder, $v_{\mathrm{xc}}(\mathbf{r},t)$, is called the time-dependent xc potential.

In the static case, the variational principle $\delta E[\rho] = 0$ was used to derive an expression for the static xc potential. In the time-dependent case one instead has the condition that the action A is stationary, $\delta A[\rho] = 0$, with:

$$A[\rho] = \int_{t_0}^{t_1} dt\langle\Psi[\rho](t)|i\frac{\partial}{\partial t} - \hat{H}(t)|\Psi[\rho](t)\rangle. \tag{45}$$

Because of the 1-1 mapping between $\Psi(\mathbf{r},t)$ and $\rho(\mathbf{r},t)$ we can obtain the correct density from the Euler equation

$$\frac{\partial A[\rho]}{\partial\rho(\mathbf{r},t)} = 0 \tag{46}$$

Analogous to the HK functional F_{HK} one can define a universal density functional and an xc part of A, A_{xc}. The time-dependent xc potential its functional derivative:

$$v_{\mathrm{xc}}(\mathbf{r},t) = \frac{\partial A_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r},t)} \tag{47}$$

1. The adiabatic approximation

For slowly-varying external potentials one can show that:

$$A_{\mathrm{xc}} = \int_{t_0}^{t_1} E_{\mathrm{xc}}[\rho_t]dt \tag{48}$$

where ρ_t is the density at time t. In the *adiabatic approximation* the TD xc potential simplifies to:

$$v_{\mathrm{xc}}[\rho](\mathbf{r},t) = \frac{\delta A_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r},t)} \approx \frac{\delta E_{\mathrm{xc}}[\rho_t]}{\delta\rho_t(\mathbf{r})} = v_{\mathrm{xc}}[\rho_t](\mathbf{r}) \tag{49}$$

In other words, the time-dependent xc potential is identical to the ordinary, static xc potential of DFT, but evaluated at the density at time t. Similarly, the functional derivative of v_{xc}, called f_{xc}, which we will need later, simplifies to the derivative of the static xc potential in this approximation:

$$f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',t,t') \approx \delta(t-t')\frac{\delta v_{\mathrm{xc}}^{\mathrm{stat}}(\mathbf{r})}{\delta\rho(\mathbf{r}')}. \tag{50}$$

In almost all applications of TDDFT this adiabatic approximation has been invoked for the simple reason that no reliable time-dependent xc kernels are yet available. Except for certain special cases this approximation seems to be quite reasonable. The acronym ALDA is sometimes encountered. It stands for the adiabatic approximation in combination with the local density approximation for the static xc potential.

III. GENERAL (TIME-INDEPENDENT) RESPONSE THEORY

A. Second-order perturbation theory

Consider a Hamiltonian H which consists of a part H_0 (for which the solutions $\phi_i^{(0)}$ are known) and a small perturbation H' with perturbation strength $\lambda << 1$:

$$H = H_0 + \lambda H' \tag{51}$$

The solutions of the unperturbed system are assumed to be known:

$$H_0 \phi_n^{(0)} = E_n^{(0)} \phi_n^{(0)}. \tag{52}$$

We want to find good, approximate solutions for E_n, ϕ_n for the full Hamiltonian

$$H\phi_n = E_n \phi_n. \tag{53}$$

The solutions of H_0 (which is Hermitian) form an orthonormal set

$$\langle \phi_i^{(0)} | \phi_j^{(0)} \rangle = \delta_{ij} \tag{54}$$

In perturbation theory it is assumed that the energies and eigenvectors of H can be expressed in a Taylor series with respect to λ:

$$E_n = \sum_{j=0}^{\infty} \lambda^j E_n^{(j)} \tag{55}$$

$$\phi_n = \sum_{j=0}^{\infty} \lambda^j \phi_n^{(j)}. \tag{56}$$

This leads to:

$$(H_0 + \lambda H')(\phi_n^{(0)} + \lambda \phi_n^{(1)} + \lambda^2 \phi_n^{(2)} + \ldots) = \tag{57}$$

$$(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(\phi_n^{(0)} + \lambda \phi_n^{(1)} + \lambda^2 \phi_n^{(2)} + \ldots) \tag{58}$$

Equating powers of λ left and right (for the first order) yields

$$H_0 \phi_n^{(1)} + H' \phi_n^{(0)} = E_n^{(0)} \phi_n^{(1)} + E_n^{(1)} \phi_n^{(0)} \tag{59}$$

EXERCISE: the $(2n + 1)$-rule of perturbation theory.

- A) By left multiplication with $\phi_n^{(0)*}$ and integration over all coordinates, derive $E_n^{(1)} = \langle \phi_n^{(0)} | H' | \phi_n^{(0)} \rangle$
- B) Write down the expressions for the λ^2 and λ^3 terms.
- C) Similar to A) derive explicit expressions for $E_n^{(2)}$ and $E_n^{(3)}$.
- D) Show that $E_n^{(3)}$ can be determined from first-order quantities ($\phi_n^{(1)}$, $E_n^{(1)}$) only.

- E) (Optional): Show that $E^{(2k+1)}$ can be determined from the knowledge of $\{\phi_n^0 \dots \phi_n^{(k)}\}$ and $E_n^{(0)} \dots E_n^{(k)}$.

If one expands the first-order wave functions in the basis of the unperturbed functions

$$\phi_n^{(1)} = \sum_k a_{nk}^{(1)} \phi_k^{(0)}, \tag{60}$$

one can derive the ground-state energy expression up to second order:

$$E_0 = E_0^{(0)} + \langle \phi_0^{(0)} | H' | \phi_0^{(0)} \rangle + \sum_{k \neq 0} \frac{\langle \phi_0^{(0)} | H' | \phi_k^{(0)} \rangle \langle \phi_k^{(0)} | H' | \phi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}} \tag{61}$$

In the case of two different perturbations H^1 and H^2 the two terms H' in the 2nd order perturbation term have to be replaced by H^1 and H^2 respectively (and a term with H^1 and H^2 interchanged has to be added).

B. Second-order molecular properties

For a mixed second derivative in the energy, we have

$$E_0^{(2)} = \sum_{k \neq 0} \frac{H_{0k}^1 H_{k0}^2 + H_{0k}^2 H_{k0}^1}{E_0 - E_k} \tag{62}$$

Note that if ($H^1 = H^2$) this will always give an energy lowering because $E_k > E_0$.

For the case $H^1 = Fz, H^2 = Fx$, we have

$$E_0^{(2)} = F^2 \sum_{k \neq 0} \frac{z_{0k} x_{k0} + x_{0k} z_{k0}}{E_0 - E_k}. \tag{63}$$

This is proportional to α_{xz} $(+\alpha_{zx})$, the xz-component ($+zx$-component) of the static polarizability tensor. In fact the energy change due to a static uniform electric field F is usually written as:

$$\Delta E = -\sum_{\alpha} \mu_\alpha F_\alpha - \frac{1}{2!} \sum_{\alpha\beta} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{3!} \sum_{\alpha\beta\gamma} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{4!} \sum_{\alpha\beta\gamma\delta} \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots \tag{64}$$

This defines the static polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ) tensors. However, note that experimentalists usually employ a different definition of β and γ, due to a different prefactor (factor 2 for β and factor 6 for γ).

We obtain the sum-over-states expression for the static polarizability:

$$\alpha_{xz} = -2E_0^{(2)}/E^2 = 2 \sum_{k \neq 0} \frac{z_{0k} x_{k0}}{E_k - E_0} \tag{65}$$

Similar expressions exist for the magnetizability (2nd derivative with respect to uniform magnetic field) and for many more properties.

Perturbation 1	**Perturbation 2**	**Name**	**Effect**
Magn. Fld	Magn. Fld	Magnetizability	
El. Fld	El. Fld	Polarizability (α)	Rayleigh scattering
Magn. Fld	El. Fld	magnetic-electric (α)	Optical activity, CD
El. Fld	Nucl. displ.	Atomic Polar tensor	IR intensities
Nucl. displ.	Nucl. displ.	Force Const. matrix	IR freq., normal modes
Magn. Fld	Nucl. displ.	Atomic Axial tensor	Vibrational CD
2 El. Flds	Nucl. displ.	normal-mode der. of α	Raman int.
Magn. field	Magn. mom. on nucl.		NMR
Nucl. Magn. mom.	Nucl. Magn. mom.		spin-spin coupl.

The response theory treated here is more generally applicable than just electric fields. Also magnetic perturbations and nuclear displacements can be treated. However, for magnetic effects one has to take gauge dependence into account and in case of nuclear displacements the basis functions depend upon the perturbation (because they move along with the displaced atom). This makes electric perturbations the simplest ones.

C. Coupled perturbed Hartree-Fock and KS equations

Here, the analytic solution of second order molecular properties in the Hartree–Fock (HF) or KS theories will be briefly treated starting from the matrix form of the SCF equations of HF or DFT (see Ref. [5]). Denoting the Fock (KS) matrix by F, the density matrix by P, the one-electron part of F by h and the Coulomb and exchange (or xc) part by $G(P)$ (it depends on the density matrix), we can write:

$$F = h + G(P). \tag{66}$$

The converged result is obtained when the Fock and density matrix commute:

$$FP - PF = 0 \tag{67}$$

If we now introduce a perturbation (such as static external field) with strength λ, we can expand all matrices in different orders of this perturbation:

$$P = P^{(0)} + P^{(1)} + ... \tag{68}$$

and similarly for the other matrices. Taking together the first order terms one has

$$F^{(0)}P^{(1)} - P^{(1)}F^{(0)} + F^{(1)}P^{(0)} - P^{(0)}F^{(1)} = 0 \tag{69}$$

There is an additional constraint: the density matrix should be idempotent. That leads to

$$P^{(0)}P^{(1)} + P^{(1)}P^{(0)} = P^{(1)} \tag{70}$$

This shows that the first-order density matrix must have only occ-virt and virt-occ blocks and that these blocks should be the transpose (for x real) of each other.

$$P^{(1)} = x + x^{\dagger}, \qquad x = (1 - P^{(0)})MP^{(0)}. \tag{71}$$

Here M is arbitrary $(1 - P^{(0)})$ is a projection operator on the virtual subspace and $P^{(0)}$ on the occupied subspace.

After some algebra, this leads to

$$F^{(0)}x - xF^{(0)} + (1 - P^{(0)})F^{(1)}P^{(0)} = 0 \tag{72}$$

Writing x in terms of occupied and virtual HF or KS orbitals ($x = \sum_{i,a} P_{ia}^{(1)} \phi_i \phi_a$) leads to (again after some algebra)

$$x_{ia} = \frac{F_{ia}^{(1)}}{\varepsilon_i - \varepsilon_a} \tag{73}$$

Because $F^{(1)}$ depends on P (so also on x) this is usually solved iteratively, starting from, for example, $x = 0$.

D. Sum-over-states versus finite field versus analytic solution

1. Finite-field calculations

Because the static polarizability tensor is determined by a second-order change in the energy it can be determined by performing energy calculations at various electric fields. This is convenient as it can be applied to any method which calculates the energy of the system. An alternative (for the polarizability) would be to take the first derivative of the dipole moment with respect to a electric perturbation:

$$\alpha_{xz} = -2 \lim_{F_x \to 0, F_z \to 0} \frac{(E(F_x, F_z))}{F_x F_z} = \lim_{F_x \to 0} \frac{(\mu_z(F_x))}{F_x} = \lim_{F_z \to 0} \frac{(\mu_x(F_z))}{F_z} \tag{74}$$

In a *variational* theory, like HF or DFT, these two approaches will yield identical results in principle. However, in MP2, for example, these two expressions are not identical, which gives some arbitrariness for α (usually one takes the energy derivative).

The main advantage of finite-field (FF) methods has been mentioned already, they are almost universally applicable. The disadvantages are important however.

- Numerically difficult, many accurate digits needed in a calculation. This is especially problematic in DFT where one uses numerical integration to calculate the xc terms.
- Only *static* properties are accessible, not time-dependent properties.
- A lot of handwork (calculations with many different external fields have to be combined to obtain the desired property tensor).

2. Sum-over-state (SOS) approaches

In an SOS calculation for the polarizability (or other properties) one exploits the expression in terms of the exact eigenfunctions and excited state energies of the system (similar expressions exist for hyperpolarizabilities and other properties):

$$\alpha_{xz} = 2\sum_{k\neq 0} \frac{z_{0k}x_{k0}}{E_k - E_0}. \tag{75}$$

In the frequency-dependent case this expression will also contain the frequency ω.

The advantage is that this can be done immediately if one has a method which provides these quantities, such as CIS or various semi-empirical approaches like INDO, etc. The disadvantages are:

- The sum includes all the continuum states.
- Often many terms in the sum have a nonnegligible contribution, which means many excited states are needed. Also the convergence pattern with respect to increasing number of excitations may be very irregular, which makes it unclear how reliable the results are.

The SOS approach is particularly useful if only a few terms are important in the SOS expression. In that case one can employ a few-level model, of which the 2-level model is the simplest variant.

For the average β this takes the simple form:

$$\beta \propto (\mu_{ee} - \mu_{gg})\frac{\mu_{ge}^2}{E_{ge}^2}, \tag{76}$$

where $\mu_{ee}, \mu_{gg}, \mu_{ge}, E_{ge}$ are the excited state dipole moment, ground state dipole moment, transition dipole moment and excitation energy, respectively. This is often used for the description of hyperpolarizability of push-pull systems, where a large hyperpolarizability often originates from one charge-transfer excitation in a donor-acceptor molecule. In that case the knowledge of the properties of only this single excited state provides a qualitative understanding of why the hyperpolarizability is (or is not) large.

3. Analytic, density-matrix based

This is the approach usually called coupled-perturbed HF (or KS) in the static case and TDHF or TDDFT in the time-dependent case. The main disadvantage is that it requires a significant amount of programming. Its advantages are that it is easy to use (technically accurate in contrast to FF), it gives results identical to FF (if both are carefully performed), time-dependent properties and static properties are calculated in the same framework (i.e. the static limit of the TD results will give the FF result). In terms of the density matrix P of the molecule, the dipole moment in direction x is obtained from

$$\mu_x = \mathrm{Tr}[xP] = \sum_i [xP]_{ii} = \sum_{i,j} x_{ij}P_{ji} \tag{77}$$

The polarizability, the linear change in the dipole moment due to an electric field is obtained from the linear change in the density matrix δP due to the field:

$$\alpha_{ij} = \mathrm{Tr}[r^i \delta P^j] = \sum_a [r^i \delta P^j]_{aa} = \sum_{a,b} r^i_{ab}\delta P^j_{ab} \tag{78}$$

Similarly one could get the second-order change in the dipole moment (the first hyperpolarizability) from

$$\beta_{ijk} = \mathrm{Tr}[r^i \delta P^{jk}] = \sum_a [r^i \delta P^{jk}]_{aa} = \sum_{a,b} r^i_{ab} \delta P^{jk}_{ab} \tag{79}$$

and so on. However, because of the $(2n+1)$-rule there are more efficient ways to obtain the hyperpolarizability tensor.

By considering the (change in the) expectation value of the electric quadrupole or higher multipole moments, one can also calculate the electric dipole-electric quadrupole polarizability tensor once δP^j is known. Similarly one can calculate the mixed magnetic electric polarizability, and so on. Turning this around: if the density change due to a external quadrupole field is known, the change in the expectation value of the dipole moment gives the electric quadrupole - electric dipole polarizability. This is an example of the interchange rule, which shows two routes to mixed derivatives.

IV. TIME-DEPENDENT LINEAR RESPONSE

A. General linear response (exact eigenfunctions)

See Refs. [6,5] for further details.

1. Pictures

We will need different pictures of quantum mechanics in the following. In the usual Schrödinger picture (operators like r and p time-independent, wavefunctions time-dependent) one has

$$i\frac{\partial}{\partial t}|\Psi_S(t)\rangle = \hat{H}|\Psi_S(t)\rangle \tag{80}$$

which has the formal solution:

$$|\Psi_S(t)\rangle = e^{-i\hat{H}(t-t_0)}|\Psi_S(t_0)\rangle \tag{81}$$

If the Hamiltonian consists of two parts H_0 and H' where the solutions to H_0 are known, it can be useful to work in the interaction picture, which is defined by:

$$|\Psi_I(t)\rangle = e^{i\hat{H}_0(t)}|\Psi_S(t)\rangle \tag{82}$$

Exercise: proof that the time-evolution of $|\Psi_I(t)\rangle$ is determined by

$$i\frac{\partial}{\partial t}|\Psi_I(t)\rangle = \hat{H}'(t)|\Psi_I(t)\rangle \tag{83}$$

$$\hat{H}'(t) = e^{iH_0t}\hat{H}'e^{-iH_0t} \tag{84}$$

Finally, in the Heisenberg picture,

$$|\Psi_H(t)\rangle = e^{i\hat{H}(t)}|\Psi_S(t)\rangle \tag{85}$$

the state vector is time-independent ($\frac{\partial}{\partial t}|\Psi_H(t)\rangle = 0$), and the operators are time-dependent.

2. Interacting and noninteracting density-density response functions

Consider a Hamiltonian which consists of a time-independent part H_0 and a time-dependent perturbation $H'(t)$ which is switched on at $t = 0$

$$H = H_0 + H'(t), \tag{86}$$

where

$$H'(t) = 0 \qquad (t < 0) \tag{87}$$

$$H'(t) = \int d\mathbf{r}\rho(\mathbf{r},t)v^{\mathrm{ext}}(\mathbf{r},t) \qquad (t > 0) \tag{88}$$

$$\tag{89}$$

We would like to know how the expectation value of an operator A changes in time by the influence of the external perturbation. The change in the operator at time t is given by:

$$\delta A = \delta\langle A\rangle(t) = \langle\Psi(t)|A|\Psi(t)\rangle - \langle\Psi_0|A|\Psi_0\rangle, \tag{90}$$

where $|\Psi_0\rangle$ is the solution for the Hamiltonian H_0 (situation before $t = 0$) and $|\Psi(t)\rangle$ is the solution for the Hamiltonian $H_0 + H'(t)$.

It is convenient to introduce solutions in the Heisenberg picture with respect to H_0:

$$|\Psi_H(t)\rangle = e^{-i\hat{H}_0(t)}|\Psi_S(t)\rangle \tag{91}$$

The time evolution of this wave function in the Heisenberg picture is then given by:

$$i\frac{\partial}{\partial t}|\Psi_H(t)\rangle = \hat{H}'_H|\Psi_H(t)\rangle \tag{92}$$

(Exercise: show that $(H')_H$ is related to $(H')_S$ by $(H')_H = e^{iH_0t}(H')_S e^{-iH_0t}$). Consequently, the time evolution of $|\Psi_H(t)\rangle$ can be written as

$$|\Psi_H(t)\rangle = |\Psi_0\rangle - i\int_0^t dt' \left[\hat{H}'(t')\right]_H |\Psi_H(t)\rangle \tag{93}$$

This can be solved iteratively by inserting the equation for $|\Psi_H(t)\rangle$ repeatedly on the right hand side. If we are interested in linear terms only:

$$|\Psi_H(t)\rangle = |\Psi_0\rangle - i\int_0^t dt'(\hat{H}'(t'))_H|\Psi_0\rangle + O((H')^2) \tag{94}$$

In *linear* response theory we are interested only in the linear effect of H'. The idea is that H' represents a small perturbation on the system and that terms of the order of $(H')^2$ are usually negligible (except of course if one is interested in properties like hyperpolarizabilities!).

This expression allows us to calculate the expectation value of A as a function of time:

$$\begin{aligned}
\langle\Psi_H(t)|A(t)|\Psi_H(t)\rangle &= \langle\Psi_0|A_H(t)|\Psi_0\rangle - i\int_0^t dt'\langle\Psi_0|A_H(t)\hat{H}'(t'))_H|\Psi_0\rangle \qquad (95)\\
&+ i\int_0^t dt'\langle\Psi_0|(\hat{H}'(t'))_H A_H(t)|\Psi_0\rangle\rangle + O(H')^2) \qquad (96)\\
&\approx \langle\Psi_0|A_H|\Psi_0\rangle - i\int_0^t dt'\langle\Psi_0|[A_H, \hat{H}'_H(t')]|\Psi_0\rangle \qquad (97)
\end{aligned}$$

For the *change* in the expectation value we get:

$$\delta A(t) = -i\int_0^t dt'\langle\Psi_0|[A_H(t), \hat{H}'_H(t')]|\Psi_0\rangle \tag{98}$$

If we are interested in the linear change of the density, $\delta\rho(\mathbf{r}, t)$, due to a perturbation

$$\hat{H}'_H(t) = \int d\mathbf{r}\rho_H(\mathbf{r}, t)v^{\text{ext}}(\mathbf{r}, t) \tag{99}$$

we obtain

$$\delta\rho(\mathbf{r},t) = \int_0^\infty dt' \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}',t,t') v^{\text{ext}}(\mathbf{r}',t'). \tag{100}$$

Here $\chi(\mathbf{r},\mathbf{r}',t,t')$ is given by

$$\chi(\mathbf{r},\mathbf{r}',t,t') = -i\Theta(t-t')\langle\Psi_0|[\rho(\mathbf{r},t)_H, \rho(\mathbf{r}',t')_H]|\Psi_0\rangle \tag{101}$$

and is called the *density-density response function* or sometimes the generalized susceptibility. The Heaviside function $\Theta(t)$ is equal to 1 for $t \geq 0$ and 0 for $t < 0$ and allows us to extend the time integration range to infinity (it assures the causality principle is obeyed).

Now we can use the resolution of the identity

$$\sum_m |\Psi_m\rangle\langle\Psi_m| = 1, \tag{102}$$

where the sum runs over all eigenstates (including continuum states) and rewrite

$$\begin{aligned}\langle\Psi_0|[\rho(\mathbf{r},t)_H, \rho(\mathbf{r}',t')_H]|\Psi_0\rangle = & \sum_m [\langle\Psi_0|\rho(\mathbf{r},t)_H|\Psi_m\rangle\langle\Psi_m|\rho(\mathbf{r}',t')_H|\Psi_0\rangle & (103)\\ & - \langle\Psi_0|\rho(\mathbf{r}',t')_H|\Psi_m\rangle\langle\Psi_m|\rho(\mathbf{r},t)_H|\Psi_0\rangle]\,. & (104)\end{aligned}$$

We insert the density in the Schrödinger picture again to rewrite

$$\begin{aligned}\langle\Psi_0|[\rho(\mathbf{r},t)_H, \rho(\mathbf{r}',t')_H]|\Psi_0\rangle = & \sum_m \Big[\langle\Psi_0|e^{iH_0t}\rho(\mathbf{r})_S e^{-iH_0t}|\Psi_m\rangle\langle\Psi_m|e^{iH_0t'}\rho(\mathbf{r}')_S e^{-iH_0t'}|\Psi_0\rangle & (105)\\ & - \langle\Psi_0|e^{iH_0t'}\rho(\mathbf{r}')_S e^{-iH_0t'}|\Psi_m\rangle\langle\Psi_m|e^{iH_0t}\rho(\mathbf{r})_S e^{-iH_0t}|\Psi_0\rangle\Big]\,. & (106)\end{aligned}$$

Because Ψ_0 and Ψ_m are eigenfunctions of H_0 this reduces to:

$$\begin{aligned}\langle\Psi_0|[\rho(\mathbf{r},t)_H, \rho(\mathbf{r}',t')_H]|\Psi_0\rangle = & \sum_m \Big[e^{i(E_0-E_m)(t-t')}\langle\Psi_0|\rho(\mathbf{r})_S|\Psi_m\rangle\langle\Psi_m|\rho(\mathbf{r}')_S|\Psi_0\rangle & (107)\\ & - e^{i(E_0-E_m)(t'-t)}\ \langle\Psi_0|\rho(\mathbf{r}')_S|\Psi_m\rangle\langle\Psi_m|\rho(\mathbf{r})_S|\Psi_0\rangle] & (108)\end{aligned}$$

which shows that $\chi(\mathbf{r},\mathbf{r}',t,t')$ depends only on the time difference $(t-t')$, which is physically clear, because the results should not depend on the arbitrary choice of the zero point in time. We obtain finally for the linear density-density response function in the time domain:

$$\begin{aligned}\chi(\mathbf{r},\mathbf{r}',t-t') = -i\Theta(t-t') & \sum_m \Big[e^{i(E_0-E_m)(t-t')}\langle\Psi_0|\rho(\mathbf{r})|\Psi_m\rangle\langle\Psi_m|\rho(\mathbf{r}')|\Psi_0\rangle & (109)\\ & - e^{i(E_m-E_0)(t-t')}\langle\Psi_0|\rho(\mathbf{r}')|\Psi_m\rangle\langle\Psi_m|\rho(\mathbf{r})|\Psi_0\rangle\Big]\,. & (110)\end{aligned}$$

A Fourier transform with respect to $(t-t')$ yields the response function in its frequency representation:

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_m \frac{\langle\Psi_0|\rho(\mathbf{r})|\Psi_m\rangle\langle\Psi_m|\rho(\mathbf{r}')|\Psi_0\rangle}{\omega-(E_m-E_0)} - \frac{\langle\Psi_0|\rho(\mathbf{r}')|\Psi_m\rangle\langle\Psi_m|\rho(\mathbf{r})|\Psi_0\rangle}{\omega+(E_m-E_0)} \tag{111}$$

[If we would have started from an external potential which is switched on infinitely slowly ($e^{\eta t}v^{\text{ext}}(\mathbf{r},t)$) we would have obtained a positive infinitesimal in the denominator ($\omega \to \omega + i\eta$).]

The convolution theorem:

$$a(t) = \int_{-\infty}^{\infty} dt' b(t-t')c(t') \longrightarrow \tilde{a}(\omega) = \tilde{b}(\omega)\tilde{c}(\omega) \tag{112}$$

implies that we can write the Fourier transformed equation as

$$\delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}',\omega) v_{\text{ext}}(\mathbf{r}',\omega). \tag{113}$$

Clearly, the response function has the excitation energies as poles. This means that a determination of the response function gives access to the excitation energies.

In case of a noninteracting particle system (KS or HF) the wavefunctions are Slater determinants built from the KS (HF) orbitals. The density operator is simply a delta function. The Slater rule for one-electron operators is:

$$\langle\Psi_0|H|\Psi_I\rangle = \langle\phi_i|h|\phi_a\rangle \tag{114}$$

where ϕ_i and ϕ_a are the one-electron orbitals in which the ground and excited state determinants differ (if they differ by more than one, the matrix element is zero). Using this, we get:

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \lim_{\epsilon\to 0} \sum_{i,a} \frac{\phi_i^*(\mathbf{r})\phi_a(\mathbf{r})\phi_a^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\omega - (\varepsilon_a - \varepsilon_i) + i\epsilon} - \frac{\phi_i^*(\mathbf{r}')\phi_a(\mathbf{r}')\phi_a^*(\mathbf{r})\phi_i(\mathbf{r})}{\omega + (\varepsilon_a - \varepsilon_i) + i\epsilon} \tag{115}$$

B. Linear density response in TDDFT

In normal response theory the first-order density change $\delta\rho(\mathbf{r},\omega)$ is obtained from the interacting response function χ and the external perturbation v_{ext}:

$$\delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}',\omega) v_{\text{ext}}(\mathbf{r}',\omega) \tag{116}$$

Similarly, the first-order change in the TDDFT case is determined by the KS (noninteracting) response function χ_s acting upon the change in the KS potential, δv_s:

$$\delta\rho_s(\mathbf{r},\omega) = \int d\mathbf{r}' \chi_s(\mathbf{r},\mathbf{r}',\omega) \delta v_s(\mathbf{r}',\omega) \tag{117}$$

Because of the TD HK theorem, we know (assume!) that there exists a unique δv_s such that the density changes in the interacting and noninteracting particle systems will be identical:

$$\delta\rho(\mathbf{r},\omega) = \delta\rho_s(\mathbf{r},\omega) \tag{118}$$

We would like to determine what δv_s looks like. It is equal to the difference in the TD KS potential for the unperturbed system [with density $\rho_0(\mathbf{r})$] and the TD KS potential for the perturbed system, specified by the density $\rho_0(\mathbf{r}) + \delta\rho(\mathbf{r},t)$. Remembering that the KS potential is given in terms of the density as:

$$v_s(\mathbf{r},t) = v_{\text{ext}}(\mathbf{r},t) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}(\mathbf{r},t) \tag{119}$$

$$\delta v_s(\mathbf{r},t) = v_s[\rho_0+\delta\rho](\mathbf{r},t) - v_s[\rho_0](\mathbf{r},t) \tag{120}$$

$$= \left[v_0(\mathbf{r}) + v_{\text{ext}}(\mathbf{r},t) + \int d\mathbf{r}' \frac{\rho_0(\mathbf{r}',t)+\delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}[\rho_0+\delta\rho](\mathbf{r},t)\right] \tag{121}$$

$$- \left[v_0(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho_0(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}[\rho_0](\mathbf{r},t)\right] \tag{122}$$

From the functional derivative of v_{xc}, this results in:

$$\delta v_s(\mathbf{r},t) = v_{\text{ext}}(\mathbf{r},t) + \int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r}' \int dt' \frac{\delta v_{\text{xc}}(\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')}|_{\rho=\rho_0} \delta\rho(\mathbf{r}',t'), \tag{123}$$

where $\delta v_{\text{xc}}/\delta\rho$ is called f_{xc}, the exchange-correlation kernel.

To summarize, the exact density change to an external time-dependent perturbation $v_{\text{ext}}(\mathbf{r},t)$ can be determined either from the exact response function, in shorthand notation

$$\delta\rho = \chi v_{\text{ext}} \tag{124}$$

or from the KS response function and the change in the KS potential

$$\delta\rho = \chi_s \delta v_s. \tag{125}$$

V. TDDFT EQUATIONS FOR EXCITATION ENERGIES AND POLARIZABILITIES

A. Derivation of the TDDFT equations for excitation energies and polarizabilities

From the general expression for the noninteracting response function

$$\chi_{s,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\omega) = \delta_{\sigma\sigma'}\sum_{i,a}\frac{\phi^*_{i\sigma}(\mathbf{r})\phi_{a\sigma}(\mathbf{r})\phi^*_{a\sigma}(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}')}{\omega-(\varepsilon_{a\sigma}-\varepsilon_{i\sigma})} - \frac{\phi^*_{i\sigma}(\mathbf{r}')\phi_{a\sigma}(\mathbf{r}')\phi^*_{a\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r})}{\omega+(\varepsilon_{a\sigma}-\varepsilon_{i\sigma})} \tag{126}$$

it is clear that the first order change in the density can be written in terms of products of occupied and virtual KS orbitals:

$$\delta\rho(\mathbf{r},\omega) = \sum_i^{N_{\text{occ}}}\sum_a^{N_{\text{virt}}}\sum_\sigma P_{ia\sigma}(\omega)\phi^*_{a\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) + P_{ai\sigma}(\omega)\phi_{a\sigma}(\mathbf{r})\phi^*_{i\sigma}(\mathbf{r}) \tag{127}$$

where we have employed the usual convention that i, j denote occupied orbitals, and a, b denote virtual orbitals. The occ-virt block of P is sometimes called the particle-hole (ph) block and the elements P_{ai} are referred to as hole-particle (hp).

From the relation (in short-hand notation) $\delta\rho = \chi_s\delta v_s$, we see that

$$P_{ia\sigma} = \frac{-[\delta v_s]_{ia\sigma}}{(\varepsilon_{a\sigma}-\varepsilon_{i\sigma})+\omega} \tag{128}$$

$$P_{ai\sigma} = \frac{-[\delta v_s]_{ai\sigma}}{(\varepsilon_{a\sigma}-\varepsilon_{i\sigma})-\omega} \tag{129}$$

where $[\delta v_s]_{ai\sigma}$ is $\int d\mathbf{r}'\phi^*_{a\sigma}(\mathbf{r}')\delta v_s(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}')$.

This expression can be compared directly to those for time-independent coupled perturbed HF or KS equations given earlier, to which they reduce for $\omega \to 0$. (There we explicitly proved that the first order density matrix should have the occ-virt form.)

As in the time-independent case, the problem with these equations is that the δv_s matrix elements depend upon the desired density change $\delta\rho$. There are two ways to handle this. The first approach is iterative and usually leads to a rapidly converged result for the density matrix elements $P_{ia\sigma}$. It starts from a guess for the first-order change in the Kohn–Sham potential. The external potential can be used for that. This yields approximations for $P_{ia\sigma}$ and $P_{ai\sigma}$. From that one can calculate $\delta\rho$ which is needed to get approximations for the Coulomb and xc terms in δv_s. The new approximation for δv_s yields new approximations for the density matrix elements. Using DIIS or similar techniques this yields a converged solution within a few cycles. Then the polarizability at frequency ω can be calculated.

However, this iterative approach is not the only way to go, and we will now show how the density matrix elements can be obtained directly from a set of linear equations. That set of linear equations also will lead us to an eigenvalue equation which determines the excitation energies and oscillator strengths of the system.

We first write

$$v_{s,ia\sigma} = v^{\text{ext}}_{ia\sigma} + \int d\mathbf{r}\phi^*_{i\sigma}(\mathbf{r}) \left[\int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + f^{\sigma\uparrow}_{xc}(\mathbf{r},\mathbf{r}',\omega)\delta\rho^{\uparrow}(\mathbf{r}') + f^{\sigma\downarrow}_{xc}(\mathbf{r},\mathbf{r}',\omega)\delta\rho^{\downarrow}(\mathbf{r}') \right] \phi_{a\sigma}(\mathbf{r}) \tag{130}$$

$$= v^{\text{ext}}_{ia\sigma} + \int d\mathbf{r}\phi^*_{i\sigma}(\mathbf{r}) \left[\int d\mathbf{r}' \sum_{jb\tau} \left[P_{jb\tau}(\omega)\phi^*_{b\tau}(\mathbf{r}')\phi_{j\tau}(\mathbf{r}') + P_{bj\tau}(\omega)\phi_{b\tau}(\mathbf{r}')\phi^*_{j\tau}(\mathbf{r}') \right] \right. \tag{131}$$

$$\left. \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f^{\sigma\tau}_{xc}(\mathbf{r},\mathbf{r}',\omega) \right) \right] \phi_{a\sigma}(\mathbf{r}) \tag{132}$$

$$= v^{\text{ext}}_{ia\sigma} + \sum_{jb\tau} [K_{ia\sigma,jb\tau}P_{jb\tau} + K_{ia\sigma,bj\tau}P_{bj\tau}], \tag{133}$$

where

$$K_{ia\sigma,jb\tau} = \int\int d\mathbf{r}d\mathbf{r}'\phi^*_{i\sigma}(\mathbf{r})\phi_{a\sigma}(\mathbf{r}) \left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f^{\sigma\tau}_{xc}(\mathbf{r},\mathbf{r}',\omega) \right] \phi_{j\tau}(\mathbf{r}')\phi^*_{b\tau}(\mathbf{r}'), \tag{134}$$

to arrive at

$$\sum_{bj\tau} [\delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\varepsilon_{a\sigma} - \varepsilon_{i\sigma} + \omega) + K_{ia\sigma,jb\tau}] P_{jb\tau} + \sum_{bj\tau} K_{ia\sigma,bj\tau}P_{bj\tau} = -v^{\text{ext}}_{ia\sigma} \tag{135}$$

$$\sum_{bj\tau} [\delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\varepsilon_{a\sigma} - \varepsilon_{i\sigma} - \omega) + K_{ai\sigma,jb\tau}] P_{jb\tau} + \sum_{bj\tau} K_{ai\sigma,bj\tau}P_{bj\tau} = -v^{\text{ext}}_{ai\sigma} \tag{136}$$

Using TDHF notation this gives

$$\left\{ \begin{bmatrix} A(\omega) & B(\omega) \\ B^*(\omega) & A^*(\omega) \end{bmatrix} - \omega \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \right\} \begin{pmatrix} X \\ Y \end{pmatrix} = - \begin{pmatrix} V^{\text{ext}}(\omega) \\ V^{\text{ext},*}(\omega) \end{pmatrix}, \tag{137}$$

where

$$X_{jb\tau} = P_{jb\tau} \tag{138}$$

$$Y_{jb\tau} = P_{bj\tau} \tag{139}$$

$$A_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ab}\delta_{ij}(\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) + K_{ia\sigma,jb\tau} \tag{140}$$

$$B_{ia\sigma,bj\tau} = K_{ia\sigma,bj\tau} \tag{141}$$

For a particular external perturbation V we now have a set of coupled equations from which we can extract $P_{ia\sigma}$, the density change and a variety of molecular properties, starting with the frequency-dependent polarizability.

As is well-known, $\alpha(\omega)$ has poles at the excitation energies of the system. This should somehow be reflected in the equations above. At the poles, the system exhibits resonant behavior, i.e. a infinitely small external perturbation has a huge effect on the density change. This can only occur if the matrix on the left has a zero eigenvalue (is not invertible) at the excitation energy. In other words:

$$\begin{bmatrix} A(\omega) & B(\omega) \\ B(\omega) & A(\omega) \end{bmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \tag{142}$$

The TDHF equations for excitation energies have the same form, except that the f_{xc} matrix elements have to be replaced by exchange matrix elements in that case. The TDHF equations are slightly more complicated for that reason than the TDDFT equations in the adiabatic approximation.

If we assume a closed-shell system, where $\phi_{m\uparrow} = \phi_{m\downarrow}$ for all m, these matrix equations can be split in separate singlet and triplet problems by the unitary transformation

$$u_{ia} = \frac{1}{\sqrt{2}}(P_{ia\uparrow} + P_{ia\downarrow}) \tag{143}$$

$$v_{ia} = \frac{1}{\sqrt{2}}(P_{ia\uparrow} - P_{ia\downarrow}) \tag{144}$$

Assuming real orbitals we can rewrite:

$$(A - B)(A + B)(X + Y) = \omega^2(X + Y) \tag{145}$$

This reduces the dimension of the problem by a factor of two. The problem is still non-Hermitian though. Because $(A - B)$ is trivial (diagonal) in adiabatic TDDFT, we can rewrite once again:

$$(A - B)^{1/2}(A + B)(A - B)^{1/2}(X + Y)' = \omega^2(X + Y)' \tag{146}$$

$$\Omega F_i = \omega_i^2 F_i, \tag{147}$$

where $(X + Y)' = (A - B)^{-1/2}(X + Y)$ has been introduced. The remaining equation has the form of a standard Hermitian eigenvalue problem. In case of a symmetric molecule this problem blocks out: each irrep gets its own block. This may again reduce the computational expense drastically.

The eigenvalue equation may be solved directly with a standard diagonalization routine. However, the linear dimension of Ω is $N^{\mathrm{occ}}N^{\mathrm{virt}}$, the cost of a diagonalization is proportional to N^3, which results in N^6 scaling. The same is true for the straight-forward solution of the set of linear equations for the density matrix elements. Both are too expensive for application to medium-sized or large molecules. Besides the CPU problem there is also a memory problem with the Ω-matrix.

Fortunately the eigenvalue equation can be solved iteratively by the Davidson or Lanczos methods, where typically one is interested in the few lowest excitation energies of a certain irrep. This is the most frequent case, because these are usually the excitations in the visible spectrum. Then the time-determining step is the matrix-(test)vector product $\Omega \cdot v$, which scales like N^3 (or better if linear scaling techniques are applied). This makes the cost of an excitation energy or polarizability comparable to that of an SCF.

The approximation $B = 0$ is known as the Tamm-Dancoff Approximation (TDA), which is also called CI Singles (CIS) in the TDHF formalism. In the TDHF case, this simplifies the equations somewhat at the cost of an additional approximation. It basically decouples the particle-hole and hole-particle blocks of the matrices.

B. Calculating the polarizability.

For the polarizability, we need only the real part of the density change, as given by, $2\Re\delta P = X + Y$. Starting from

$$\left\{\begin{bmatrix} A(\omega) & B(\omega) \\ B(\omega) & A(\omega) \end{bmatrix} - \omega \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}\right\} \begin{pmatrix} X \\ Y \end{pmatrix} = - \begin{pmatrix} V^{\text{ext}}(\omega) \\ V^{\text{ext},*}(\omega) \end{pmatrix}, \tag{148}$$

we obtain:

$$AX + BY + \omega X = -[V^{\text{ext}}] \tag{149}$$

$$BX + AY - \omega Y = -[V^{\text{ext}}]^* \tag{150}$$

Summing and subtracting the two equations leads (for a real perturbation like an electric field) to

$$(A+B)(X+Y) + \omega(X-Y) = -2\Re V^{\text{ext}} \tag{151}$$

$$(A-B)(X-Y) + \omega(X+Y) = 0, \tag{152}$$

which gives

$$\left[(A+B) - \omega^2(A-B)^{-1}\right](X+Y) = -2\Re V^{\text{ext}} \tag{153}$$

$$\left[(A+B) - \omega^2(A-B)^{-1}\right]\Re(\delta P) = -\Re V^{\text{ext}} \tag{154}$$

Defining $S = (A-B)^{-1}$

$$S^{-1/2}\left[(A+B) - \omega^2 S\right] S^{-1/2} S^{1/2} \Re(\delta P) = -S^{-1/2}\Re V^{\text{ext}} \tag{155}$$

$$\left[S^{-1/2}(A+B)S^{-1/2} - \omega^2\right] S^{1/2}\Re(\delta P) = -S^{-1/2}\Re V^{\text{ext}} \tag{156}$$

$$\Re(\delta P) = -S^{1/2}\left[S^{-1/2}(A+B)S^{-1/2} - \omega^2\right]^{-1} S^{-1/2}\Re V^{\text{ext}} \tag{157}$$

Finally one obtains

$$(\Re\delta P)(\omega) = S^{-1/2}\left\{\omega^2\mathbf{1} - \Omega(\omega)\right\}^{-1} S^{-1/2} V^{\text{ext}}(\omega) \tag{158}$$

where

$$\Omega(\omega) = -S^{-1/2}(A+B)S^{-1/2}, \tag{159}$$

where Ω is the matrix of the previous section. As a result, we obtain for the polarizability tensor component α_{xz}

$$\alpha_{xz}(\omega) = 2\vec{x}^{\dagger}\left\{S^{-1/2}\left[\Omega(\omega) - \omega^2\mathbf{1}\right]^{-1} S^{-1/2}\right\}\vec{z} \tag{160}$$

In the adiabatic approximation Ω is frequency independent and we can replace the inverse with the spectral representation of this operator,

$$\left[\Omega(\omega) - \omega^2\mathbf{1}\right]^{-1} = \sum_I \frac{\vec{F}_I\vec{F}_I^{\dagger}}{\omega_I^2 - \omega^2}, \tag{161}$$

where $\vec{F}_I$ and ω_I^2 are the eigenvectors and eigenvalues of Ω, respectively. (This expression can be checked by acting on an arbitrary vector as a linear combination of $\vec{F}_I$). Comparing the resulting expression shows that

$$\vec{x}^\dagger S^{-1/2}\vec{F}_I = \omega_I^{1/2}\langle\Psi_0|\hat{x}|\Psi_I\rangle \tag{162}$$

Recalling the SOS expression for α

$$\alpha_{xz}(\omega) = 2\sum_I \frac{(E_I - E_0)\langle\Psi_0|\hat{x}|\Psi_I\rangle\langle\Psi_I|\hat{z}|\Psi_0\rangle}{(E_I - E_0)^2 - \omega^2} \tag{163}$$

$$\omega_I = E_I - E_0 \tag{164}$$

$$f_I = \frac{2}{3}\omega_I(|\langle\Psi_0|\hat{x}|\Psi_I\rangle|^2 + |\langle\Psi_0|\hat{y}|\Psi_I\rangle|^2 + |\langle\Psi_0|\hat{z}|\Psi_I\rangle|^2) \tag{165}$$

$$\alpha_{\mathrm{av}}(\omega) = \sum_I \frac{f_I}{\omega_I^2 - \omega^2} \tag{166}$$

we obtain an expression for the oscillator strength of excitation I:

$$f_I = \frac{2}{3}\left(|\vec{x}^\dagger S^{-1/2}\vec{F}_i|^2 + y + z\right) \tag{167}$$

In a complete basis the oscillator strengths satisfy the Thomas-Reiche-Kuhn (TRK) sum rule

$$\sum_I f_I = N_e, \tag{168}$$

where N_e is the number of valence electrons.

C. Example: the H$_2$ molecule in minimal basis

This example was taken from Casida [10]. If we only have an s function on atom A and an s function on atom B, the MOs can only be:

$$\phi_g(\mathbf{r}) = \frac{s_A(\mathbf{r}) + s_B(\mathbf{r})}{\sqrt{2(1 + \langle s_A|s_B\rangle)}} \tag{169}$$

$$\phi_u(\mathbf{r}) = \frac{s_A(\mathbf{r}) - s_B(\mathbf{r})}{\sqrt{2(1 - \langle s_A|s_B\rangle)}} \tag{170}$$

$$\tag{171}$$

If we define $\varepsilon_{\mathrm{gap}} = \varepsilon_u - \varepsilon_g$, the eigenvalue equation, which has dimension $N^{\mathrm{occ}}N^{\mathrm{virt}}N^{\mathrm{spin}} = 1 \times 1 \times 2$ looks like this:

$$\begin{bmatrix} \varepsilon_{\mathrm{gap}}^2 + 2\varepsilon_{\mathrm{gap}}K_{\uparrow\uparrow} & 2\varepsilon_{\mathrm{gap}}K_{\uparrow\downarrow} \\ 2\varepsilon_{\mathrm{gap}}K_{\downarrow\uparrow} & \varepsilon_{\mathrm{gap}}^2 + 2\varepsilon_{\mathrm{gap}}K_{\downarrow\downarrow} \end{bmatrix} \vec{F}_I = \omega_I^2\vec{F}_I \tag{172}$$

Switching to another basis, using u and v from the previous section (Eq. 144) leads to a 1×1 matrix for the singlet-singlet problem and a 1×1 matrix for the singlet-triplet problem. Also without this transformation it is easily verified that the solutions to this eigenvalue equation are:

$$F_S = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{173}$$

$$F_T = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}, \tag{174}$$

where the subscripts S and T already hint at the fact that these are the singlet and triplet excitations respectively. (It is clear that a symmetric vector like F_S does not change the total up and down spin densities.) The excitation energies are given by

$$\omega_S = \sqrt{\varepsilon_{\text{gap}}(\varepsilon_{\text{gap}} + 2(K_{\uparrow\uparrow} + K_{\uparrow\downarrow}))} \approx \varepsilon_{\text{gap}} + K_{\uparrow\uparrow} + K_{\uparrow\downarrow} \tag{175}$$

$$\omega_T = \sqrt{\varepsilon_{\text{gap}}(\varepsilon_{\text{gap}} + 2(K_{\uparrow\uparrow} - K_{\uparrow\downarrow}))} \approx \varepsilon_{\text{gap}} + K_{\uparrow\uparrow} - K_{\uparrow\downarrow} \tag{176}$$

$$, \tag{177}$$

where we have used that $K_{\uparrow\uparrow} = K_{\downarrow\downarrow}$, $K_{\downarrow\uparrow} = K_{\downarrow\uparrow}$. The approximation is valid if the K-matrix elements are small corrections to the orbital energy differences.

These expressions give some support for the often used interpretation of KS orbital energy differences as approximate excitation energies. Furthermore they provide a very efficient way to estimate TDDFT excitation energies, by calculating a simple matrix element. This approach is known as the *Single Pole Approximation.* It works reasonably well if, i) there is little mixing between different one-orbital excitations $\phi_{1,occ} \rightarrow \phi_{3,virt}$ and $\phi_{2,occ} \rightarrow \phi_{3,virt}$ (in case of two occupied levels) and ii) the K matrix element is small compared to the orbital energy difference.

Another, slightly better but equally inexpensive, approximation can be used: the diagonal approximation, which is just the expression under the square root in the previous equations, without the Taylor expansion of the square root. This does not assume that the K matrix elements are small, but still assumes diagonal dominance for the Ω_S and Ω_T matrices (in other words: no mixing of one-electron excitations). It also requires only a single matrix element to be calculated.

However, there are many cases where the mixing of different one-electron excitations is crucial to get a good description of the physics. We shall give examples on porphyrins, where the low intensity of the Q-bands and high intensities of the B-bands is explained from precisely such mixing.

For this reason, the approximations just mentioned are not widely used in quantum chemical programs. The alternative, the iterative solution of the full matrix equation is not very expensive computationally, so there is little reason to introduce new approximations.

VI. PRACTICAL ASPECTS OF RESPONSE PROPERTY CALCULATIONS

A. Basis set considerations

For calculations on (high-lying) excitation energies and (hyper)polarizabilities, larger than normal basis sets may be required for reliable results than are needed in ground-state calculations like geometry optimizations. The reason is that high-lying virtuals (which in fact provide a discrete representation of the continuum) are important for those properties, whereas they are not important for normal calculations. In order to obtain a good description one needs *diffuse* functions. Another way of putting this is to say the the (hyper)polarizabilities probe the outer region of the molecule.

An example of basis set effects is shown in Tab. I where the excitation energies and (hyper)polarizability of CO is shown. It should be clear that such large effects are to be expected mainly for small molecules. For larger molecules the important excitations involve usually the low-lying virtuals (the outer region also becomes relatively unimportant). For example, the α and γ values for polymers can be well described by ordinary double-zeta basis functions if one considers the tensor components along the molecular axis. For the accurate description of tensor components perpendicular to the molecular axis diffuse functions may still be needed, because there is no basis set sharing in this case.

Another example is given in Tab. II, where basis set effects are studied for the low-lying excitation energies of free base porphin. Good convergence is observed already with standard basis sets such as the double-zeta-polarized basis set III.

B. Different methods for calculating excitation energies

There are many methods available for calculating excitation energies. They differ wildly in computational cost and in the accuracy of the results.

On the accurate end of the scale one has the multi-reference CI and coupled-cluster methods, with a computational scaling of N^6 or worse. These methods can be used for accurate results on small molecules and for calibration of more approximate and cheaper methods.

Somewhat less well-known approaches are the solution of the so-called GW and Bethe-Salpeter equations, which is popular in solid-state physics, but which have only recently been applied with some success to molecules. The same is true for Quantum Monte Carlo which is a potentially very accurate method, as it makes no assumptions on the form of the wavefunction. It also has been applied only recently to molecular excited states with interesting results, but too few to enable a definite assessment.

Next in line are perhaps the SAC-CI, CASPT2, MRMP, STEOM-CC and TDDFT methods. The Symmetry-Adapted-Cluster-CI method by Nakatsuji and coworkers is basically a CI in which not all determinants are taken into account. The rules by which it is decided which determinants can be ignored introduce a slight arbitrariness and this approach is therefore somewhat less *ab initio* than the methods mentioned before. However, the great advantage is that it enables calculations on large systems. Applications to molecules with about 100 atoms have already been shown.

The CASPT2 (complete-active-space second-order perturbation theory) by Roos and coworkers and MRMP (Multi-reference Möller-Plesset) by Hirao and coworkers methods are based on CASSCF. The CASSCF method is a cheaper variant of MCSCF which scales like N^5 with system size. The MCSCF excitation energies should improve over TDHF, but in many cases dynamic correlation is important (transition metal compounds) and the CASSCF/MCSCF excitation energies may be off by several eV. MRMP and CASPT2 solve this problem. The typical error of these methods is in the order of 0.2 eV. An important advantage is that they also treat double excitations. The system size which can be treated depends strongly on the number of active orbitals. A system like MnO_4^- cannot yet be treated by CASPT2 because too many active orbitals have to be taken into account. However, successful applications to porphyrines have already been demonstrated. Chemical intuition from the user is required because it is crucial for the reliability of the results that the correct active orbitals are identified. Furthermore some technical knowledge of the algorithm is also required because there may be a problem with intruder states which is not so easy to get rid of. This restricts the practical usefulness of CASPT2 somewhat to expert users.

The STEOM-CC (similarity-transformed equation-of-motion coupled-cluster method) is a modification of the ordinary EOM-CC method (usually at singles and doubles level) intended to be much more efficient (by Nooijen and coworkers). Certain approximations are made in this process which in some cases make the results less reliable. Initial results are promising but further testing seems needed for a definite assessment.

TDDFT is computationally cheaper than the methods in the same list (formally $O(N^3)$, closer to $O(N)$ with distance cut-offs). Many tests have been performed. In many normal cases, TDDFT performs quite well and is of similar accuracy to the methods just mentioned. The method is easy to use, technically. The only freedom of choice is for the xc functionals. As in the ground-state case, popular functionals like B3LYP perform well. Special xc potentials have also been devised for use in TDDFT calculations. These usually perform very well. Some problems have not yet been solved in TDDFT (in other words: the current xc functionals are not always good enough). A serious problem in linear chains has been identified where polarizabilities are (strongly) overestimated and excitation energies underestimated. Another problem is that double excitations cannot be predicted yet, although, surprisingly, excitations with a considerable amount of double excitation character are often still quite well described in practice. The lowest singlet excitation in dissociating H_2 is incorrectly described, which should give a warning for application to some types of potential energy surface calculations. There may be a triplet instability problem for triplet excitation energies.

The TDHF method is of similar expense as TDDFT (formally N^4). The results are much poorer in standard cases. It shares the problems of TDDFT (except the linear chain problem). There are not so many other cases where TDHF is to be preferred over TDDFT.

Semi-empirical methods come in various varieties (ZINDO/S, INDO, MNDO, etc.). They usually include a single or double CI and may be especially parametrized for spectroscopic applications (as indicated by /S). They are inexpensive, but are somewhat risky to use outside the domain for which the parameters have been optimized. In particular applications to difficult systems containing transition metals may fail.

TABLES

TABLE I. Basis set effects on α, β, ω_i

BASIS	α	β	$^1\Sigma_+$	$^1\Pi$
II (DZ)	10.200	9.7564	14.24	8.58
III (DZP)	11.017	6.8376	13.97	8.76
V (TZ2P)	11.472	14.599	12.61	8.57
VI (TZ3P)	12.689	22.316	11.25	8.57
VI1DIFF (TZ3P+1diff)	12.979	23.790	11.37	8.55
VI2DIFF (TZ3P+2diff)	13.010	23.394	10.77	8.55
VI3DIFF (TZ3P+3diff)	13.012	23.177	10.80	8.55
Ref.	13.08	26.6	10.78	8.51

TABLE II. Basis set effects on BP/ALDA dipole-allowed singlet excitation energies and oscillator strengths of free base porphin up to 5.6 eV in the experimental geometry

Sym.	Nr.	SZ(I)[a]		DZ(II)[a]		DZP(III)[a]		TZP(IV)[a]		TZ2P(V)[a]		TZ2PAE(V,ae)[a]	
B_{1u}	1	2.32	0.001	2.99	0.001	3.10	0.0004	3.10	0.0005	3.08	0.0005	3.08	0.0005
	2	5.46	0.004	5.94	0.001	5.91	0.002	5.21	0.003	5.22	0.003	5.22	0.003
B_{2u}	1	2.46	0.001	2.37	0.0006	2.31	0.00005	2.29	0.0000003	2.29	0.000002	2.29	0.000009
	2	3.26	0.03	3.04	0.03	2.92	0.03	2.95	0.05	2.95	0.05	2.95	0.05
	3	4.00	1.150	3.59	1.081	3.51	1.026	3.46	0.9985	3.47	1.002	3.46	1.000
	4	4.54	0.135	4.10	0.1	4.04	0.08	4.05	0.08	4.05	0.08	4.05	0.08
	5	5.63	0.05	5.27	0.06	5.18	0.04	5.16	0.07	5.17	0.07	5.17	0.07
	6	5.81	0.102	5.41	0.04	5.35	0.05	5.32	0.07	5.33	0.07	5.33	0.07
	7	5.90	0.1068	5.65	0.1	5.50	0.08	5.35	0.05	5.37	0.05	5.36	0.05
	8	6.24	0.002	5.87	0.006	5.71	0.0004	5.63	0.0005	5.64	0.0004	5.64	0.0004
B_{3u}	1	2.02	0.03	2.13	0.02	2.10	0.1	2.09	0.008	2.10	0.008	2.10	0.007
	2	3.00	0.02	2.88	0.03	2.80	0.04	2.83	0.07	2.83	0.07	2.83	0.07
	3	3.80	0.440	3.59	0.826	3.51	0.797	3.47	0.7722	3.48	0.7811	3.48	0.7793
	4	4.27	0.02	3.95	0.03	3.93	0.02	3.94	0.01	3.94	0.02	3.94	0.02
	5	4.50	0.824	4.32	0.448	4.22	0.4265	4.21	0.415	4.22	0.4059	4.21	0.4079
	6	5.78	0.384	5.46	0.06	5.33	0.05	5.30	0.1299	5.31	0.1255	5.31	0.1264
	7	5.95	0.01	5.63	0.1689	5.52	0.1659	5.43	0.1359	5.44	0.1345	5.44	0.1357
	8	6.47	0.1006	6.01	0.1018	5.84	0.063	5.71	0.02	5.71	0.02	5.71	0.02

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[a] STO basis sets from the ADF basis set database were used. SZ, DZ, DZP, TZP, TZ2P, TZ2PAE are, respectively, short for valence single zeta, valence double zeta, valence double zeta with a polarization function, valence triple zeta with a polarization function, valence triple zeta with two polarization functions, and finally all-electron valence triple zeta with two polarization functions. In parentheses the ADF names for these basis sets are given.

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