TIME-DEPENDENT DENSITY-FUNCTIONAL RESPONSE THEORY FOR MOLECULES

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ABSTRACT

Time-dependent density-functional response theory (TD-DFRT) is presented from the point of view of quantum chemistry. The extension of density-functional theory (DFT) into the time-domain is reviewed from the point of view of Runge, Gross, and Kohn. The basic working equations of TD-DFRT are then derived in a form analogous to the time-dependent Hartree–Fock (TDHF) equations used for molecular calculations. This is the first practical formulation of TD-DFRT for molecular applications, and the equations are presented in a more general form than has been the case for either atoms or solids. In particular, the present TD-DFRT equations anticipate applications to open-shell molecules based on spin-unrestricted DFT equations with fractional occupation numbers, and are general enough to accept time-dependent exchange-correlation functionals beyond the adiabatic approximation. The use of auxiliary function techniques to eliminate the four-center integrals that arise in TD-DFRT is discussed. The simple example of H_2 is used to illustrate the TD-DFRT method and its relationship to TDHF and to the usual *ad hoc* ΔSCF-based DFT treatment of excited states. The TD-DFRT method set forth here provides a powerful DFT technique for the calculation of such optical properties as dynamic polarizabilities and electronic excitation spectra, and can be readily extended to treat a number of other properties such as hyperpolarizabilities and intermolecular forces.

Contents

I. Introduction

Density functional theory (DFT) has become increasingly popular in the quantum chemistry community due to the rather good quality of results for a wide variety of molecular properties, combined with its computational efficiency. However, molecular applications of DFT have been limited to the calculation of static properties, thus excluding many problems in molecular optics and electronic spectroscopy which involve time-dependent fields, because none of the previously existing molecular algorithms could handle time-dependent DFT. The present chapter gives a molecular algorithm for time-dependent density functional response theory.

The popular Kohn–Sham formulation of DFT provides a computationally convenient, time-independent, Hartree–Fock (HF) like theory in which the HF exchange energy is replaced by an exchange-correlation functional. However, unlike the HF approximation, DFT leads to the exact ground state energy and density in the limit that the exchange-correlation functional becomes exact. Since no practical exact form of the exchange-correlation functional is known, it must be approximated in practice. These approximations have now reached the stage that properties calculated from DFT are often more comparable to those obtained from second-order Møller–Plesset than from the HF approximation. The advantages of DFT over other *ab initio* methods become even more pronounced when the multiplicative nature of the DFT exchange-correlation potential is exploited to simplify computations. This advantage is realized in fully numerical atomic DFT calculations, and in DFT algorithms for solids which use plane wave bases and fast Fourier transform techniques, as well as in molecular DFT codes which use auxiliary functions to eliminate the need to calculate costly four-center integrals, thereby obtaining a nominal scaling of N^3 with the size of the basis set, as opposed to the nominal scaling of N^4 for HF. Thus, when efficiently implemented, DFT can be used to study larger molecules than is possible with other *ab initio* methods.

However, the Hohenberg–Kohn–Sham formulation of DFT is time-independent, and thus does not cover the treatment of problems involving time-dependent fields, as are encountered in many problems in molecular optics and spectroscopy. Although time-independent DFT has been used to calculate excitation energies via a ΔSCF (Δself-consistent-field)-based approach, this is difficult to justify formally and entails practical difficulties as well. In the first instance, such a calculation basically assumes that the same functional used to determine the ground state energy and charge density can be used to calculate the excited state energy and charge density. ΔSCF excitation energies are then calculated by simply performing two DFT SCF calculations, one with the ground and the other with an excited state configuration, and then taking the energy difference. Since a Hohenberg–Kohn theorem can be derived for the lowest state of each symmetry, this approach may be partially justified for these states provided any symmetry-dependence of the exchange-correlation functional is ignored (see Ref. [1] pp. 204-205.) However, the problem of justifying the ΔSCF method becomes severe for spin and spatial multiplets which have different energies but the same charge density. In this case, it is clear that the energy is not a functional of the excited-state charge density alone. The usual *ad hoc* solution [2,3] is to assume that the ΔSCF procedure only applies to excited states which are well described by a single-determinant wave function. First-order expressions for multiplet energies are then sought, on the basis of an assumed zero-order form of the excited-state wave functions, in terms of the energies of single-determinant states, together with a minimum number of electron-repulsion integrals when the energies of single-determinant states are not sufficient. (See Section VI for an example of this ΔSCF-based DFT approach to excited states.) This procedure has been partially automated [3] and a similar method has been used for estimating oscillator

strengths [4]. Aside from the problems of justification and the need to make assumptions about the form of the excited state wave function, other principal problems with the method include the need to calculate bielectronic integrals which are not normally present in DFT, the need to converge one or more separate SCF calculations for each excited state, and the problem that symmetry breaking may occur (see, for example, the case of acetylene in Ref. [5]) which can make state assignment difficult if not impossible. Even though convergence and symmetry breaking problems may be reduced by using the transition state method [6] to estimate ΔSCF excitation energies, the remaining problems mean that this approach is at best cumbersome for calculating electronic excitation spectra.

The DFT calculation of static electrical response properties is much more straightforward. In this case, there is no problem with the formal justification. Since the exact ground state charge density is obtained, in the limit of the exact exchange-correlation functional, properties such as polarizabilities and hyperpolarizabilities which depend on the response of the charge density to an applied static electric field also become exact in this limit. This is in contrast to the algorithmically similar HF theory which is fundamentally approximate. Of course, in practice, the quality of static response properties calculated using DFT depends upon the quality of the approximate exchange-correlation functional used. A number of studies of molecular dipole polarizabilities and hyperpolarizabilities [5,7–14] along with previous work on atoms and solids (reviewed in Ref. [15]), have found that modern DFT gives results for these properties that are often significantly better than HF results.

Calculations of static electric response properties can be carried out in either of two different fashions. In the finite field method, the energy or dipole moment is calculated as a function of the strength of a perturbing potential introduced into the SCF orbital Hamiltonian. Polarizabilities and hyperpolarizabilities are then calculated by numerical differentiation or by fitting of the field-induced energy or dipole moment. This is a simple method to implement but requires careful attention to numerical errors in order to obtain accurate hyperpolarizabilities [10]. The alternative to the finite field method is to take the necessary derivatives with respect to the field strength analytically. This leads to the coupled Kohn–Sham (CKS) equations, which are identical to the static density-functional response theory equations. This is more involved to program but is numerically more stable than the finite-field method. The calculations of the dipole polarizabilities of rare gas and other closed shell atoms by Stott and Zaremba [16] and by Mahan [17] are often cited as the first implementations of static density-functional response theory, although earlier work based upon the Xα method was carried out by Ahlberg and Goscinski [18]. Most static density-functional response theory calculations have been for atoms or other systems with spherical symmetry and have been carried out with one of two algorithms. Both the Green-function method of Stott and Zaremba [16] and the modified Sternheimer method of Mahan [17] were developed specifically for systems with spherical symmetry, and neither is suitable for density-functional calculations of molecular response properties. However, the CKS equations also arise in the calculation of analytic second derivatives of molecular potential energy surfaces. Formal equations for this purpose have been presented by Fournier [19], Dunlap and Andzelm [20], and Komornicki and Fitzgerald [21]. Colwell, Murray, Handy and Amos have presented CKS equations in the context of calculating molecular dipole polarizabilities and hyperpolarizabilities and have implemented them in CADPAC (the Cambridge Analytical Derivative Package) [13]. All of these approches are restricted to treating the response to a *static* field.

The calculation of dynamic response properties rests upon the extension of DFT into the time domain. A formal foundation for this extension has been laid by many workers, most notably Ghosh and Deb [22,23], Bartolotti [24,25], and Runge, Gross, Kohn, and others [26–30], who have shown how many of the important concepts of time-independent DFT

can be generalized in a rigorous manner to treat problems involving local, time-dependent external potentials. This allows the treatment of time-dependent electric fields as well as some magnetic effects. Thus it is adequate for treating many problems in optics and spectroscopy where magnetic field effects are small. The formal development of time-dependent DFT actually postdated the first applications of time-dependent density-functional response theory (TD-DFRT), which was first done simply as an *ad hoc* extension of static density-functional response theory, somewhat in the spirit of the time-dependent Hartree–Fock (TDHF) approximation. Because of its flexibility and its simplicity, TD-DFRT remains the most important method for implementing time-dependent DFT and constitutes a powerful method for calculating not only dynamic polarizabilities and hyperpolarizabilities, but also excitation spectra and a number of other properties as well. The earliest application of TD-DFRT is probably that of Zangwill and Soven [31] who used the method to calculate rare gas photoabsorption cross-sections. This was soon followed by atomic TD-DFRT calculations of other photoabsorption spectra [32] and van der Waals coefficients [33] and by solid state TD-DFRT calculations of frequency-dependent dielectric constants [34,35]. The method is now well-established for atoms and solids, and a review has been given by Mahan and Subbaswamy [15]. The method has also become popular for studying the optical properties of metal clusters [36] where it is applied either in the context of the jellium sphere model [37–41] or the spherically-averaged pseudopotential model [42–44].

In contrast to the electrical and optical response properties just mentionned, the full formal treatment of (static or dynamic) magnetic response properties, such as nuclear magnetic resonance (NMR) chemical shifts, in DFT is more involved. In this case, a fundamental extension of the DFT formalism to the case of nonlocal (velocity-dependent) external potentials is required. This formal extension has been developed in the form of current-density functional theory (CDFT) (see Ref. [45] for a review). Practical CDFT response equations have been given for the static case by Colwell and Handy [46], and an indication of the CDFT treatment in the dynamic case is given in the present chapter (at the end of Sec. II). The CDFT response equations reduce to the (static or dynamic) density-functional response theory equations with an external vector potential if the current-density terms are neglected. It is interesting to note that at this level of approximation the coupling cancels out in the linear response to a magnetic field, leaving only the "independent particle" term. The results for NMR chemical shifts are already quite good in the independent particle approximation [47], and the agreement with experiment can be further improved using only a small *ad hoc* correction [48]. It will be very interesting to see tests of current-density functionals, as well as the size of the current-density contributions, when these results become available.

The present paper focuses on electrical response properties and optical properties, specifically dynamic polarizabilities and excitation spectra. By definition, electrical response properties are independent of the magnetic field*. For the optical properties, the magnetic field of the photon is negligible for most practical purposes, and will be neglected here, as it is in most other *ab initio* methods for treating optical properties. Since magnetic fields are not being treated, a rigorous development of TD-DFRT can be given without recourse to current-density functional theory.

The algorithms used for the applications of TD-DFRT mentionned above depend strongly upon the type of system studied. Atomic applications are based on time-dependent extensions of either the Green-function [31] or modified Sternheimer [17] methods previously mentionned in the context of static calculations. (A good introduction to the two methods

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*For example, $\alpha = [\partial \vec{\mu}(\vec{\mathcal{E}}, \vec{B})/\partial \vec{\mathcal{E}}]_{\vec{\mathcal{E}} = \vec{B} = 0}$.

can be found in Ref. [15].) These are also the methods used for the models of metal cluster optical properties mentionned above. They rely heavily on the use of spherical symmetry to reduce the three-dimensional problem to the solution of one-dimensional differential equations. Nevertheless the same basic algorithm has also been applied to calculate the time-dependent response properties of (nonsphericalized) N_2 and C_2H_2 by using single-center expansions [49,50]. However, due to the notorious unsuitability of single-center expansions for molecular calculations, this approach is of no practical utility. Algorithms used for solids [34,35] are also quite specialized and cannot be adopted directly for molecules.

The present paper lays out, in some detail, a TD-DFRT method for molecular applications. The method is in some ways analogous to molecular implementations of TDHF but differs in some important respects, notably the computational advantages of DFT, and the fact that TD-DFRT becomes exact in the limit of the exact exchange-correlation functional while the TDHF method is always an approximation. Furthermore, the usual derivation of TDHF is done in terms of an N-electron wavefunction, so this approach is inappropriate for DFT. Thus a different tack is taken in the present work, and the TD-DFRT equations are derived using a functional-derivative approach. The same functional-derivative technique can also be used to derive the TDHF equations. The present work provides a formally well-founded and convenient method for DFT calculations of spectra and other dynamic response properties. Although only dynamic polarizabilities and excitation spectra are discussed here, other properties including hyperpolarizabilities and van der Waals coefficients may also be obtained. We are implementing this method as a post-deMon program DynaRho [51].

This chapter presents TD-DFRT with a view toward practical molecular applications. Thus it includes a review not only of the formal foundations, but also of the auxiliary-function technique used in our implementation of TD-DFRT in a molecular code, as well as a simple example where the equations can be solved analytically. Although the reader is assumed to be familiar with time-independent DFT and second-quantization, the paper is intended to be relatively self-contained. A review of the formal foundations of time-dependent DFT is given in the next section. This is followed by a review of the usual wavefunction formulation of time-dependent response theory in Section III. This sets the stage for a derivation of the basic working equations of TD-DFRT in a form suitable for molecular applications, in Section IV. The use of auxiliary functions to simplify the evaluation of integrals appearing in TD-DFRT is discussed in Section V. The formalism and its relation to TDHF and to the ΔSCF-based treatment of excited states in DFT is illustrated for H_2 in Section VI. Section VII gives a summary.

II. Formal foundations

The classic Hohenberg–Kohn–Sham formulation of density functional theory is restricted to the time-independent case. Thus the treatment of time-dependent systems requires a generalization of the basic formalism of DFT to the time-dependent case. This development has been pursued by a number of authors [22–30,52,53], providing time-dependent analogs of the Hohenberg–Kohn theorems and Kohn–Sham equation. The brief synopsis of the essential elements of the time-dependent theory given here is based primarily on the work of Runge and Gross [27] and Gross and Kohn [30]. The extension, due to Ghosh and Dhara [54], of time-dependent DFT to treat time-dependent magnetic fields via current-density functional theory is also briefly discussed.

Consider an N-electron system described by the Schrödinger equation (in hartree atomic units),

$$\hat{H}(t)\Psi(t) = i\frac{\partial}{\partial t}\Psi(t)\,, \tag{2.1}$$

with Hamiltonian

$$\hat{H}(t) = \hat{T} + U + V(t) \tag{2.2}$$

where

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 \tag{2.3}$$

is the kinetic energy,

$$U = \sum_{i<j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2.4}$$

is the electron repulsion, and

$$V(t) = \sum_{i=1}^{N} v(\mathbf{r}_i, t) \tag{2.5}$$

is the external potential, assumed constant for $t < t_0$. Thus we may think of a system interacting with a time-dependent field switched on at time t_0. Note that, as usual in DFT, the restriction to external potentials which are multiplicative operators precludes a full treatment of magnetic effects, for which current-density functional theory is more appropriate. The focus here is on electric fields. The first problem is to obtain (time-dependent) expectation values as functionals of the time-dependent charge density. To this end, Runge and Gross [27] showed that the time-dependent charge density, ρ, determines the wave function up to a time-dependent phase factor[†],

$$\Psi(t) = e^{-i\phi(t)}\Psi[\rho, \Psi_0](t)\,, \tag{2.6}$$

where Ψ_0 denotes the initial condition $\Psi(t_0)$. More specifically, they showed that the external potential, $v(\mathbf{r}, t)$, is determined by the charge density, ρ, up to a spatially constant time-dependent function c(t), provided that ρ arises from a system with initial state Ψ_0 and that the external potential (*i*) can be represented as the electric potential due to a normalizable charge distribution, and (*ii*) has a time dependence which can be expressed in a Taylor's series about $t = t_0$. Equation (2.6) follows as a consequence. The proof of the Runge-Gross theorem proceeds by first showing that the external potential is determined by the current density, and then showing that the current density can be eliminated in favor of the charge density alone, provided a suitable boundary condition is satisfied. Although Xu and Rajagopal [55] pointed out a difficulty with the elimination of the current density in Runge and Gross's original formulation of this theorem [27], the clarification of condition (*i*) above by Gross and Kohn [30] and Dhara and Ghosh [56] has resolved this problem.

[†]In this notation, functionals are distinguished by the use of square brackets while the independent variables of a function appear in parentheses. Thus $\Psi[\rho, \Psi_0](t)$ indicates that Ψ is both a functional of the functions $\rho(\mathbf{r}, t)$ and $\Psi_0(\mathbf{r})$, and a function of t.

Gross and Kohn [30] also note that the conditions of the Runge–Gross theorem are not strictly satisfied in time-dependent response theory, because of the difficulty of expanding $v(\mathbf{r}, t)$ about $t_0 = -\infty$, as should be done when the perturbation is turned on adiabatically starting at $t = -\infty$. In addition, the restriction to an electric potential due to a normalizable charge distribution excludes the *exact* representation of a uniform field. However, these remarks only concern idealizations involved in the theory, not the physical systems it is intended to model. Thus they do not constitute limitations on the applicability of a response formulation of time-dependent DFT to physical fields (e.g. due to a large but finite charged plate) introduced at some finite time in the distant past.

If it is further assumed, as is usual in response theory, that the initial state Ψ_0 is a stationary ground state, then Ψ_0 is completely determined by the initial charge density, $\rho_0 = \rho(t_0)$, according to the first Hohenberg–Kohn theorem [57], provided Ψ_0 is also nondegenerate. (Of course, any initial degeneracy can usually be lifted by a small perturbation, so the degeneracy question is not a major concern.) Hence Ψ_0 can be eliminated from Eq. (2.6) so that Ψ is then determined up to a phase factor by ρ alone. For an operator $\hat{O}(t)$ which may be a function of time but which contains no derivative or integral operators on t, this phase factor cancels out on taking the expectation value. Thus expectation values are functionals only of ρ,

$$\langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle = O[\rho](t), \tag{2.7}$$

analogous to the time-independent case.

The role of the second Hohenberg–Kohn theorem, in the time-independent case, is filled, in the time-dependent theory, by a variational principle involving the action,

$$A = \int_{t_0}^{t_1} \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle \, dt. \tag{2.8}$$

The true time-dependent density is the one which makes the action stationary,

$$0 = \frac{\delta A}{\delta \rho(\mathbf{r}, t)} = \int_{t_0}^{t_1} \langle \frac{\delta \Psi(t')}{\delta \rho(\mathbf{r}, t)} | i \frac{\partial}{\partial t'} - \hat{H}(t') | \Psi(t') \rangle \, dt' + \text{c.c.}. \tag{2.9}$$

The expectation value in Eq. (2.8) is not of the form required for the phase factor to cancel out as in Eq. (2.7). Nevertheless, it is easy to see that in this case the effect of the phase factor is simply to contribute an additive constant,

$$A = \int_{t_0}^{t_1} \langle \Psi[\rho](t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi[\rho](t) \rangle \, dt + \phi(t_1) - \phi(t_0) = A[\rho] + \text{const}. \tag{2.10}$$

Thus the time-dependent density determines the action, up to an additive constant. Of course, when the variational condition (2.9) is used, the additive constant is immaterial, so this provides the analog of the second Hohenberg–Kohn theorem, for the the time-dependent theory.

The action functional can be rewritten as

$$A[\rho] = B[\rho] - \int_{t_0}^{t_1} \int v(\mathbf{r}, t) \rho(\mathbf{r}, t) \, d\mathbf{r} dt, \tag{2.11}$$

where the functional B is independent of the external potential v. A time-dependent Kohn–Sham equation can then be derived in a manner analogous to that for the time-independent

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case by *assuming* the existence of a potential $v_{\text{eff}}(\mathbf{r}, t)$, for an independent particle system, whose orbitals $\psi_i(\mathbf{r}, t)$ yield the same charge density $\rho(\mathbf{r}, t)$ as for the interacting system,

$$\rho(\mathbf{r}, t) = \sum_i f_i |\psi_i(\mathbf{r}, t)|^2 , \tag{2.12}$$

where the f_i are orbital occupation numbers. The question of whether such a potential exists is known as the "time-dependent v-representability problem." As in the time-independent case, this problem is not entirely resolved, although $v_{\text{eff}}(\mathbf{r}, t)$ can be shown to exist [29] for adiabatically introduced perturbations whose frequency does not exceed the HOMO-LUMO gap of the unperturbed system [see the remark after Eq. (4.7)]. Mearns and Kohn [29] give examples which suggest that $v_{\text{eff}}(\mathbf{r}, t)$ will also exist for higher frequency perturbations as well, except at isolated frequencies. Assuming $v_{\text{eff}}(\mathbf{r}, t)$ does exist, then the universal functional B can be written as

$$B[\rho] = \sum_i f_i \int_{t_0}^{t_1} \langle \psi_i(t) | i\frac{\partial}{\partial t} - \frac{1}{2}\nabla^2 | \psi_i(t) \rangle \, dt - \frac{1}{2} \int_{t_0}^{t_1} \int \int \frac{\rho(\mathbf{r}_1, t)\rho(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 d\mathbf{r}_2 dt - A_{\text{xc}}[\rho]$$

$$\tag{2.13}$$

thereby defining the exchange-correlation action functional A_{xc} which plays a role analogous to the exchange-correlation energy functional in the time-independent theory. Minimizing the action (2.11) subject to the condition (2.12), results in the time-dependent Kohn–Sham equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}, t) \right] \psi_i(\mathbf{r}, t) = i\frac{\partial}{\partial t}\psi_i(\mathbf{r}, t) , \tag{2.14}$$

where

$$v_{\text{eff}}(\mathbf{r}, t) = v(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}, t) \tag{2.15}$$

and

$$v_{\text{xc}}(\mathbf{r}, t) = \frac{\delta A_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r}, t)} . \tag{2.16}$$

Although the functional A_{xc} is unknown, in the limit of an external potential which varies slowly in time it must reduce to

$$A_{\text{xc}} = \int_{t_0}^{t_1} E_{\text{xc}}[\rho_t] \, dt , \tag{2.17}$$

where E_{xc} is the exchange-correlation functional of time-independent Kohn–Sham theory, and ρ_t denotes ρ evaluated at the time t. This is known as the "adiabatic approximation." Notice that, whereas A_{xc} is a functional of a function ρ over both time and space, E_{xc} is a functional of a function ρ_t over only space (since t is fixed).

The adiabatic approximation is a local approximation in time. Like the familiar local density approximation from time-independent DFT, which is a local approximation in space, the adiabatic approximation works well beyond its domain of rigorous justification. For this reason, and due to its relative simplicity, the adiabatic approximation has come to be the

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work horse of time-dependent DFT. In the adiabatic approximation, the first derivative of A_{xc},

$$v_{\mathrm{xc}}[\rho](\mathbf{r},t) = \frac{\delta A_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r},t)} \cong \frac{\delta E_{\mathrm{xc}}[\rho_t]}{\delta\rho_t(\mathbf{r})} = v_{\mathrm{xc}}[\rho_t](\mathbf{r}),\tag{2.18}$$

is just the familiar exchange-correlation potential of time-independent DFT evaluated with the density at a particular time. (Note the difference in notation between the right and left hand sides.) Since $v_{\mathrm{xc}}(t)$ is then determined solely by the density $\rho(t)$ at the same time, the adiabatic approximation neglects all retardation effects and assumes an instantaneous reaction of the self-consistent field to temporal changes in ρ. This is particularly obvious from the second derivative of A_{xc} which gives the response of the exchange-correlation potential to a change in the charge density,

$$\frac{\delta v_{\mathrm{xc}}[\rho](\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')} \cong \delta(t-t')\frac{\delta v_{\mathrm{xc}}[\rho_t](\mathbf{r})}{\delta\rho_t(\mathbf{r}')}.\tag{2.19}$$

While the adiabatic approximation is a physically reasonable first approximation, and is useful in practical applications, it is also important to develop functionals which go beyond this approximation.

In practical applications, the derivative of the exchange-correlation potential is used to find the response of the charge density (see Section IV). Conversely, for a given system, it is possible to invert this procedure. Gross and Kohn [28,30] have done this, using the response of the charge density to obtain an expression for the derivative of v_{xc} for the homogeneous electron gas. They have suggested that this result could be used for other systems in an approximation of $\delta v_{\mathrm{xc}}/\delta\rho$ which goes beyond the adiabatic approximation to include retardation effects.

The extension of TD-DFT to handle time-dependent magnetic fields by way of CDFT has been treated by Ghosh and Dhara [54]. In the presence of a magnetic field, Eq. (2.14) becomes

$$\left\{\frac{1}{2}\left|-i\boldsymbol{\nabla}+\frac{1}{c}\boldsymbol{a}_{\mathrm{eff}}(t)\right|^2 + v_{\mathrm{eff}}(\mathbf{r},t)\right\}\psi_i(\mathbf{r},t) = i\frac{\partial}{\partial t}\psi_i(\mathbf{r},t),\tag{2.20}$$

where

$$\frac{1}{c}\boldsymbol{a}_{\mathrm{eff}}(\mathbf{r},t) = \frac{1}{c}\boldsymbol{a}(\mathbf{r},t) + \int\frac{\mathbf{j}(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta A_{\mathrm{xc}}[\rho,\mathbf{j}]}{\delta\mathbf{j}(\mathbf{r},t)}\tag{2.21}$$

and

$$v_{\mathrm{eff}}(\mathbf{r},t) = v(\mathbf{r},t) + \int\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta A_{\mathrm{xc}}[\rho,\mathbf{j}]}{\delta\rho(\mathbf{r},t)} + \frac{1}{2c^2}\left[a^2(\mathbf{r},t)-a_{\mathrm{eff}}^2(\mathbf{r},t)\right].\tag{2.22}$$

Here, $\boldsymbol{a}$ is the external vector potential and the exchange-correlation action-functional A_{xc} depends on both the charge density ρ and the current density

$$\mathbf{j}(\mathbf{r},t) = -\frac{i}{2}\sum_i f_i\left[\psi_i^*(\mathbf{r},t)\boldsymbol{\nabla}\psi_i(\mathbf{r},t) - \psi_i(\mathbf{r},t)\boldsymbol{\nabla}\psi_i^*(\mathbf{r},t)\right] + \frac{1}{c}\rho(\mathbf{r},t)\boldsymbol{a}_{\mathrm{eff}}(\mathbf{r},t).\tag{2.23}$$

Eq. (2.20) can also be written in the form

$$\left[-\frac{1}{2}\nabla^2 + \hat{u}_{\text{eff}}(\mathbf{r},t) \right] \psi_i(\mathbf{r},t) = i\frac{\partial}{\partial t}\psi_i(\mathbf{r},t) \,, \tag{2.24}$$

where

$$\hat{u}_{\text{eff}}[\rho,\mathbf{j}](\mathbf{r},t) = v(\mathbf{r},t) + \int \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta A_{\text{xc}}[\rho,\mathbf{j}]}{\delta\rho(\mathbf{r},t)}$$
$$- \frac{i}{2c}\left[\boldsymbol{\nabla}, \boldsymbol{a}_{\text{eff}}[\rho,\mathbf{j}](\mathbf{r},t) \right]_+ + \frac{1}{2c^2}a^2(\mathbf{r},t) \,. \tag{2.25}$$

The orbital equation (2.24), and the fact that both the charge and current densities are trivial functions of the density matrix, means that the development of TD-DFRT in Section IV can be generalized to include time-dependent current-density functional response theory (TD-CDFRT). Naturally, this is computationally more demanding. In particular, terms involving derivatives with respect to the current density and derivatives of the current density with respect to the density matrix have to be introduced, and simplifications due to the multiplicative nature of the TD-DFRT effective potential are lost in TD-CDFRT. Nevertheless, the effective potential, $\hat{u}_{\text{eff}}$, divides into external and self-consistent field parts, a coupling matrix can be defined in a manner analogous to Eq. (4.8), and the remaining development is very similar to that given in Section IV. In the adiabatic approximation, the TD-CDFRT coupling matrix is frequency independent, so the static result of Colwell and Handy [46] could be taken over directly. Note, however, that Colwell and Handy follow Vignale, Rasolt, and Geldart [45] in using only the paramagnetic component of the current density, and neglecting the second term in Eq. (2.21) which results from a current-current interaction [54]. Given the close interrelationship between time-dependent electric and magnetic fields, it will be a more challenging problem how to combine current-density functionals and time-dependent functionals beyond the adiabatic approximation without overcounting. Since the present paper is not concerned with magnetic fields, the details of a time-dependent current-density functional theory will not be further pursued here.

III. Time-dependent response theory

Basic time-dependent response theory is reviewed in this section in an effort to keep the present article more or less self-contained. Much of this material is also treated in standard texts on many-body physics such as Ref. [58]. The second-quantized notation used here is based upon an underlying basis set of time-independent orthonormal spin-orbitals $\psi_{i\sigma}$, where the Roman and Greek indices refer to space and spin respectively. These orbitals will eventually be taken to be the molecular orbitals of the unperturbed molecule. The corresponding annihilation operators are denoted by $\hat{a}_{i\sigma}$.

Time-dependent response theory concerns the response of a system initially in a stationary state, generally taken to be the ground state Ψ_0 unless otherwise specified, to a perturbation

$$\delta\hat{v}_{\text{appl}}(t) = \sum_{ij\sigma} \delta v_{ij\sigma}^{\text{appl}}(t)\hat{a}_{i\sigma}^\dagger\hat{a}_{j\sigma} \tag{3.1}$$

turned on slowly beginning at time $t = t_0$ sometime in the distant past. The assumption that the perturbation is turned on slowly (i.e. the adiabatic assumption) is important since otherwise transient contributions occur which depend upon the time at which the perturbation was turned on. The linear response of the density matrix

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$$\delta P_{ij\sigma}(t) = \langle \delta\Psi_0(t)|\hat{a}_{j\sigma}^\dagger \hat{a}_{i\sigma}|\Psi_0(t)\rangle + \langle \Psi_0(t)|\hat{a}_{j\sigma}^\dagger \hat{a}_{i\sigma}|\delta\Psi_0(t)\rangle \tag{3.2}$$

is conveniently expressed in terms of the generalized susceptibility χ by

$$\delta P_{ij\sigma}(t) = \sum_{kl\tau} \int_{-\infty}^{+\infty} \chi_{ij\sigma,kl\tau}(t-t')\delta v_{kl\tau}^{\mathrm{appl}}(t')\,dt'\,. \tag{3.3}$$

Introducing the Fourier transform convention

$$f(\omega) = \int_{-\infty}^{+\infty} e^{+i\omega t}f(t)\,dt\,, \qquad f(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-i\omega t}f(\omega)\,d\omega\,, \tag{3.4}$$

and making use of the convolution theorem,

$$h(t) = \int_{-\infty}^{+\infty} g(t-t')f(t')\,dt' \quad \Longleftrightarrow \quad h(\omega) = g(\omega)f(\omega)\,, \tag{3.5}$$

allows Eq. (3.3) to be rewritten as

$$\delta P_{ij\sigma}(\omega) = \sum_{kl\tau} \chi_{ij\sigma,kl\tau}(\omega)\delta v_{kl\tau}^{\mathrm{appl}}(\omega)\,. \tag{3.6}$$

To derive a formula for the generalized susceptibility, assume that the system is initially in its ground stationary state, Ψ_0, and introduce the perturbation

$$\delta\hat{w}(t) = e^{-\eta(t_1-t)}\delta\hat{v}_{\mathrm{appl}}(t) \tag{3.7}$$

where η is a positive infinitesimal. The infinitesimal enforces the adiabatic approximation in such a way that $\delta\hat{w}(t_1) = \delta\hat{v}(t_1)$. Equation (3.2) is then used with standard time-dependent perturbation theory [59] to calculate the reponse of the density matrix at time t_1. In particular, setting $t_0 = -\infty$,

$$\delta\Psi_0(t_1) = -i\sum_{I\neq 0} \Psi_I(t_1)\int_{-\infty}^{t_1} \langle \Psi_I(t)|\delta\hat{w}(t)|\Psi_0(t)\rangle\,dt\,. \tag{3.8}$$

where the

$$\Psi_I(t) = e^{-iE_I t}\Psi_I \tag{3.9}$$

are the stationary states of the unperturbed Hamiltonian. Thus Eq. (3.2) becomes

$$\delta P_{ij\sigma}(t_1) = \sum_{kl\tau} \int_{-\infty}^{+\infty} \left\{ -i\Theta(t_1-t)\sum_{I\neq 0}\left[\langle\Psi_0|\hat{a}_{j\sigma}^\dagger\hat{a}_{i\sigma}|\Psi_I\rangle\langle\Psi_I|\hat{a}_{k\tau}^\dagger\hat{a}_{l\tau}|\Psi_0\rangle e^{-i(E_I-E_0-i\eta)(t_1-t)} \right.\right.$$

$$\left.\left. - \langle\Psi_0|\hat{a}_{k\tau}^\dagger\hat{a}_{l\tau}|\Psi_I\rangle\langle\Psi_I|\hat{a}_{j\sigma}^\dagger\hat{a}_{i\sigma}|\Psi_0\rangle e^{-i(E_0-E_I-i\eta)(t_1-t)} \right] \right\}\delta v_{kl\tau}^{\mathrm{appl}}(t)\,dt\,, \quad (3.10)$$

where

$$\Theta(t_1-t) = \begin{cases} 1 & \text{for } t_1 > t \\ 0 & \text{for } t_1 < t \end{cases} \tag{3.11}$$

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is the Heaviside function. Comparison with Eq. (3.3) shows that the term in curly brackets is $\chi_{ij\sigma,kl\tau}(t_1 - t)$. Taking its Fourier transform gives the sum-over-states (SOS) representation of the generalized susceptibility[‡],

$$\chi_{ij\sigma,kl\tau}(\omega) = \sum_{I \neq 0} \left\{ \frac{\langle \Psi_0 | \hat{a}_{j\sigma}^\dagger \hat{a}_{i\sigma} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_0 \rangle}{\omega - (E_I - E_0) + i\eta} - \frac{\langle \Psi_0 | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{j\sigma}^\dagger \hat{a}_{i\sigma} | \Psi_0 \rangle}{\omega + (E_I - E_0) + i\eta} \right\} .$$

(3.12)

A special case is that of a single particle system with Schrödinger equation

$$\hat{h}\psi_{i\sigma} = \epsilon_{i\sigma}\psi_{i\sigma} .$$

(3.13)

If the particle is initially in orbital $\psi_{m\mu}$ and the unperturbed stationary states are taken as the orthonormal basis set underlying the second-quantized notation, then according to formula (3.12),

$$\chi_{ij\sigma,kl\tau}(\omega) = \delta_{\sigma,\tau}\delta_{\sigma,\mu}\delta_{i,k}\delta_{j,l}\frac{\delta_{j,m} - \delta_{i,m}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} ,$$

(3.14)

where the infinitesimal has been set equal to zero. Since the response of the density matrix of a system of N independent particles with (possibly fractional) occupation numbers $f_{i\sigma}$ is the occupation-number weighted sum of the response of the density matrices for the individual orbitals, assuming that no change in occupation number is induced by the perturbation, the generalized susceptibility is

$$\chi_{ij\sigma,kl\tau}(\omega) = \sum_{m\mu} f_{m\mu}\delta_{\sigma,\tau}\delta_{\sigma,\mu}\delta_{i,k}\delta_{j,l}\frac{\delta_{j,m} - \delta_{i,m}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})}$$

$$= \delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}\frac{f_{j\sigma} - f_{i\sigma}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} .$$

(3.15)

SOS expressions can also be derived for particular response properties. Chief among these is the dynamic dipole polarizability $\boldsymbol{\alpha}(\omega)$. For simplicity of notation, consider the (x, z)-component. This may be defined by introducing a perturbation,

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[‡]As an interesting aside, the first Hohenberg–Kohn theorem [57] says that the charge density, ρ, of a system with a nondegenerate ground state determines the external potential up to an additive constant. Hence ρ also determines the N-electron hamiltonian and so the transition energies, $E_I - E_0$, and wave functions, Ψ_0 and Ψ_I, up to unimportant phase factors, with the result that the generalized susceptibility itself may be regarded as a universal functional of the unperturbed charge density. In a sense, the ultimate objective of TD-DFRT is just to find a practical representation of this functional. The treatment of TD-DFRT given in Sec. IV comes very close to this. In fact, $\chi_{\sigma\tau}^{-1}(\mathbf{r}, \mathbf{r}'; \omega) = (\chi_s)_{\sigma\tau}^{-1}(\mathbf{r}, \mathbf{r}'; \omega) - K_{\sigma\tau}[\rho](\mathbf{r}, \mathbf{r}'; \omega)$ where χ_s is the generalized susceptibility for the Kohn–Sham reference system of noninteracting particles and $K[\rho]$ is the coupling matrix defined in Sec. IV. However, this expression does not yet give the full generalized susceptibility since it only holds for the response of the true charge density, but not the density matrix, to a local perturbation: $\delta\rho_\sigma(\mathbf{r}; \omega) = \sum_\tau \int \chi_{\sigma\tau}(\mathbf{r}, \mathbf{r}'; \omega)\delta v_\tau(\mathbf{r}', \omega)d\mathbf{r}' .$

$$\delta v_{\text{appl}}(t) = \hat{z}\mathcal{E}_z(t)\,, \tag{3.16}$$

and expanding the x-component of the dipole moment to first order in the function $\mathcal{E}_z(t)$,

$$\mu_x(t) = \mu_x + \int_{-\infty}^{+\infty} \alpha_{xz}(t - t')\mathcal{E}_z(t')\,dt' + \cdots\,, \tag{3.17}$$

where the first term on the right hand side refers to the permanent dipole moment. Then, from the convolution theorem, the Fourier transform of $\alpha_{xz}(t)$ is given by

$$\alpha_{xz}(\omega) = \frac{\delta\mu_x(\omega)}{\mathcal{E}_z(\omega)}\,, \tag{3.18}$$

where $\delta\mu_x(\omega)$ is the linear response of the dipole moment [i.e. the integral in Eq. (3.17).] Since

$$\delta\mu_x(\omega) = -\sum_{ij\sigma} x_{ji\sigma}\delta P_{ij\sigma} = -\sum_{ij\sigma,kl\tau} x_{ji\sigma}\chi_{ij\sigma,kl\tau}(\omega)z_{kl\tau}\mathcal{E}_z(\omega)\,, \tag{3.19}$$

it follows that

$$\alpha_{xz}(\omega) = -\sum_{ij\sigma,kl\tau} x_{ji\sigma}\chi_{ij\sigma,kl\tau}(\omega)z_{kl\tau}\,. \tag{3.20}$$

Making use of the expression (3.12) and the fact that

$$\langle\Psi_0|\hat{x}|\Psi_I\rangle\langle\Psi_I|\hat{z}|\Psi_0\rangle = \langle\Psi_0|\hat{z}|\Psi_I\rangle\langle\Psi_I|\hat{x}|\Psi_0\rangle \tag{3.21}$$

then leads to the SOS expression

$$\alpha_{xz}(\omega) = \sum_I \frac{2(E_I - E_0)\langle\Psi_0|\hat{x}|\Psi_I\rangle\langle\Psi_I|\hat{z}|\Psi_0\rangle}{(E_I - E_0)^2 - \omega^2}\,, \tag{3.22}$$

where once again the infinitesimal has been set equal to zero. This expression is interesting because it shows that the spectroscopic oscillator strengths,

$$f_I = \frac{2}{3}(E_I - E_0)\left(|\langle\Psi_0|\hat{x}|\Psi_I\rangle|^2 + |\langle\Psi_0|\hat{y}|\Psi_I\rangle|^2 + |\langle\Psi_0|\hat{z}|\Psi_I\rangle|^2\right)\,, \tag{3.23}$$

and excitation energies,

$$\omega_I = E_I - E_0\,, \tag{3.24}$$

are the poles and residues of the mean polarizability,

$$\bar{\alpha}(\omega) = \frac{1}{3}\text{tr }\boldsymbol{\alpha}(\omega) = \sum_I \frac{f_I}{\omega_I^2 - \omega^2}\,. \tag{3.25}$$

Evidently this formula could be used to obtain the mean dynamic polarizability in cases where accurate values of excitation energies and oscillator strengths are available. However, considering the difficulty of calculating accurate transition energies and oscillator strengths for all the continuum as well as bound states, it is much easier to calculate the polarizability directly. Thus, in the next section, the converse approach is taken: A TD-DFRT expression for the dynamic polarizability is derived, and the SOS formula (3.25) is used to obtain the excitation energies and oscillator strengths from the dynamic polarizability.

IV. Density-functional response theory

Since the (exact) Kohn–Sham orbitals yield the true charge density, any property which depends only on the density, or the response of the density, is obtained exactly, in principle, within the Kohn–Sham formalism. In particular, this includes electrical response properties such as polarizabilities, as well as excitation energies and oscillator strengths which can be obtained from the pole structure of the dynamic polarizability. At the same time, the quasi-independent particle nature of the Kohn–Sham equation means that formally exact response properties can be obtained while taking advantage of the simple, diagonal form of the generalized susceptibility for an independent particle system. This is the approach taken in time-dependent density functional response theory (TD-DFRT), using the time-dependent Kohn–Sham equation as a starting point. The resulting equations resemble those of the time-dependent Hartree–Fock (TDHF) approximation [60], since Hartree–Fock is also a quasi-independent particle formalism. In fact, as will be seen in Subsection IV B, the TDHF equations can be derived by the same functional derivative method used here, though this is not the usual approach. But, unlike Kohn–Sham theory, Hartree–Fock does not yield the true charge density, so that even exact solutions of the TDHF equations can produce only approximate response properties.

In this section, the TD-DFRT equations are derived in a form suitable for general molecular applications. This will be done in the spin-unrestricted formalism, starting from the time-dependent Kohn–Sham equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{\sigma}(\mathbf{r},t) \right] \psi_{i\sigma}(\mathbf{r},t) = i\frac{\partial}{\partial t}\psi_{i\sigma}(\mathbf{r},t)\,, \qquad (4.1)$$

where the effective potential,

$$v_{\text{eff}}^{\sigma}(\mathbf{r},t) = -\sum_{I}\frac{Z_I}{r_I} + \delta v_{\text{appl}}(\mathbf{r},t) + v_{\text{SCF}}^{\sigma}(\mathbf{r},t)\,, \qquad (4.2)$$

is the sum of the external potential, including the nuclear attraction and any applied field, $\delta v_{\text{appl}}(\mathbf{r},t)$, and a self-consistent field (SCF) term,

$$v_{\text{SCF}}^{\sigma}(\mathbf{r},t) = \int \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}'-\mathbf{r}|}\,d\mathbf{r}' + v_{\text{xc}}^{\sigma}[\rho_{\uparrow},\rho_{\downarrow}](\mathbf{r},t)\,, \qquad (4.3)$$

which depends upon the spin-up and spin-down charge densities,

$$\rho(\mathbf{r},t) = \rho_{\uparrow}(\mathbf{r},t) + \rho_{\downarrow}(\mathbf{r},t)\,, \qquad (4.4)$$

$$\rho_{\sigma}(\mathbf{r},t) = \sum_{i} f_{i\sigma}|\psi_{i\sigma}(\mathbf{r},t)|^2\,, \qquad (4.5)$$

where the $f_{i\sigma}$ are the (possibly fractional) orbital occupation numbers.

A. Linear Response of the Density Matrix

The perturbation introduced into the Kohn–Sham hamiltonian by turning on an applied field $\delta v_{\text{appl}}(\mathbf{r},t)$ is, to linear order,

$$\delta v_{\text{eff}}^{\sigma}(\mathbf{r},t) = \delta v_{\text{appl}}(\mathbf{r},t) + \delta v_{\text{SCF}}^{\sigma}(\mathbf{r},t)\,, \qquad (4.6)$$

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where $\delta v^{\sigma}_{\mathrm{SCF}}(\mathbf{r},t)$ is the linear response of the self-consistent field arising from the change in the charge density. Thus the quasi-independent particle nature of the Kohn–Sham equation means that the independent-particle form of the generalized susceptibility, Eq. (3.15), can be used, together with the perturbation $\delta v^{\sigma}_{\mathrm{eff}}(\omega)$, to write down the linear response of the Kohn–Sham density matrix to the applied field. In the basis of the unperturbed molecular orbitals (MOs),

$$\delta P_{ij\sigma}(\omega) = \frac{f_{j\sigma} - f_{i\sigma}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \delta v^{\mathrm{eff}}_{ij\sigma}(\omega) . \tag{4.7}$$

Note that $\delta P_{ij\sigma}(\omega) = 0$ for $f_{i\sigma} = f_{j\sigma}$. The linear response of the Kohn–Sham density matrix gives the linear response of the true density but not of the true density matrix. Although it would be a lengthy aside to show it here, Eq. (4.7) can be used to prove v-representability when $|\omega| < \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}$ [29].

Equation (4.7) is complicated by the fact that $\delta v^{\sigma}_{\mathrm{SCF}}(\omega)$ depends upon the response of the density matrix,

$$\delta v^{\mathrm{SCF}}_{ij\sigma}(\omega) = \sum_{kl\tau} K_{ij\sigma,kl\tau}(\omega) \delta P_{kl\tau}(\omega) , \tag{4.8}$$

where the coupling matrix,

$$
\begin{aligned}
K_{ij\sigma,kl\tau}(\omega) & \\
&= \int_{-\infty}^{+\infty} e^{+i\omega(t-t')} \frac{\partial v^{\mathrm{SCF}}_{ij\sigma}(t)}{\partial P_{kl\tau}(t')} \, d(t-t') \\
&= \int_{-\infty}^{+\infty} e^{+i\omega(t-t')} \left\{ \sum_{\mu} \iint \frac{\delta v^{\mathrm{SCF}}_{ij\sigma}(t)}{\delta\rho_{\mu}(\mathbf{r},t'')} \frac{\partial\rho_{\mu}(\mathbf{r},t'')}{\partial P_{kl\tau}(t')} \, d\mathbf{r}dt'' \right\} d(t-t') \\
&= [\psi_{i\sigma}\psi^{*}_{j\sigma}|\psi_{k\tau}\psi^{*}_{l\tau}] \\
&\quad + \int_{-\infty}^{+\infty} e^{+i\omega(t-t')} \left\{ \iint \psi^{*}_{i\sigma}(\mathbf{r})\psi_{j\sigma}(\mathbf{r}) \frac{\delta^{2}A_{\mathrm{xc}}}{\delta\rho_{\sigma}(\mathbf{r},t)\delta\rho_{\tau}(\mathbf{r}',t')} \psi_{k\tau}(\mathbf{r}')\psi^{*}_{l\tau}(\mathbf{r}') \, d\mathbf{r}d\mathbf{r}' \right\} d(t-t') ,
\end{aligned}
\tag{4.9}
$$

where the functional derivative is evaluated using the *unperturbed* spin-up and spin-down charge densities, and the inner product

$$[f|g] = \iint \frac{f^{*}(\mathbf{r})g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}d\mathbf{r}' \tag{4.10}$$

has been introduced. By using the coupling matrix, Eq. (4.7) can be rewritten as

$$\sum_{kl\tau}^{f_{k\tau} - f_{l\tau} \neq 0} \left[\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l} \frac{\omega - (\epsilon_{k\sigma} - \epsilon_{l\sigma})}{f_{l\sigma} - f_{k\sigma}} - K_{ij\sigma,kl\tau}(\omega) \right] \delta P_{kl\tau}(\omega) = \delta v^{\mathrm{appl}}_{ij\sigma}(\omega) , \tag{4.11}$$

where $f_{i\sigma} \neq f_{j\sigma}$. Solving this equation for $\delta \boldsymbol{P}(\omega)$ then allows response properties to be calculated. For example, the dynamic polarizability is given by Eq. (3.20)

$$\alpha_{xz}(\omega) = -2 \sum_{ij\sigma}^{f_{i\sigma} - f_{j\sigma} > 0} x_{ji\sigma} \left(\mathrm{Re}\,\delta P_{ij\sigma} \right)(\omega) / \mathcal{E}_{z}(\omega) , \tag{4.12}$$

where $\left(\mathrm{Re}\,\delta P_{ij\sigma} \right)(\omega)$ denotes the Fourier transform of the real part of $\delta P_{ij\sigma}(t)$, and $\delta v^{\mathrm{appl}}_{ij\sigma}$ is given by Eq. (3.16).

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B. Properties of the Coupling Matrix

It follows from Eq. (4.9) that the coupling matrix satisfies the relation

$$K_{ij\sigma,kl\tau}(\omega) = [K_{kl\tau,ij\sigma}(-\omega)]^* \tag{4.13}$$

When the MOs are real, as is the usual case in quantum chemical calculations,

$$K_{ij\sigma,kl\tau}(\omega) = K_{ij\sigma,lk\tau}(\omega) = K_{ji\sigma,lk\tau}(\omega) = K_{ji\sigma,kl\tau}(\omega). \tag{4.14}$$

This results from the fact that the self-consistent field potential in DFT is local. However, even when the MOs are real, $\boldsymbol{K}$ may not be real, because A_{xc} may be complex. Although a complete discussion of this point would take us too far afield, it is worth noting that it is related to how the continuum is treated. If the continuum is treated as in Section III, A_{xc} should be real. But if the lifetimes of continuum states are of interest, A_{xc} should be treated as complex. Here, A_{xc} will be assumed real, and lifetimes will not be discussed.

In the adiabatic approximation, the replacement

$$\frac{\delta A_{\text{xc}}}{\delta \rho_\sigma(\mathbf{r},t)\delta\rho_\tau(\mathbf{r}',t')} \rightarrow \delta(t-t')\frac{\delta E_{\text{xc}}}{\delta\rho_\sigma(\mathbf{r})\delta\rho_\tau(\mathbf{r}')} \tag{4.15}$$

results in a coupling matrix which is no longer a function of ω, and which is real when the MOs are real.

Since the equations of TD-DFRT and TDHF are very similar, it is interesting to compare the properties of the coupling matrix in the two cases. With the exception of the last line of Eq. (4.9), the equations of the previous subsection are also valid within the HF approximation. Thus the only difference between the TD-DFRT and TDHF equations is that the (local) exchange-correlation potential, v_{xc}, of DFT is replaced by the (nonlocal) HF exchange operator Σ^{x}, with the result that the second term in the derivative (4.9) is different. Thus in order to derive the TDHF equations by the same method that has been used here for TD-DFRT, it remains only to evaluate the derivative $\partial\Sigma^{\text{x}}_{ij\sigma}/\partial P_{kl\tau}$, which yields the TDHF coupling matrix,

$$K_{ij\sigma,kl\tau} = [\psi_{i\sigma}\psi^*_{j\sigma}|\psi_{k\tau}\psi^*_{l\tau}] - \delta_{\sigma,\tau}[\psi_{i\sigma}\psi^*_{k\sigma}|\psi_{j\tau}\psi^*_{l\tau}]. \tag{4.16}$$

Note that the TDHF coupling matrix is independent of ω, hermitian, and

$$K_{ij\sigma,kl\tau} = K^*_{ji\sigma,lk\tau}. \tag{4.17}$$

Furthermore $\boldsymbol{K}$ is real when the MOs are real, but even in this case,

$$K_{ij\sigma,kl\tau} \neq K_{ij\sigma,lk\tau}. \tag{4.18}$$

The TD-DFRT and TDHF coupling matrices are most similar when the adiabatic approximation is made in TD-DFRT, since in this case the TD-DFRT coupling matrix is also independent of ω, and real when the MOs are real. However, the TD-DFRT coupling matrix has more symmetry than the TDHF coupling matrix [compare Eqs. (4.18) and (4.14)], due to the fact that the DFT involves only local potentials. Thus, in the adiabatic approximation, the TD-DFRT equations are computationally simpler than are the TDHF equations. Although the adiabatic approximation will be used in Sections V and VI, the treatment given in the present section will continue to be more general.

C. Separation of Real and Imaginary Parts of δP

Since only the particle-hole (ph), $f_{i\sigma} > f_{j\sigma}$, and hole-particle (hp), $f_{i\sigma} < f_{j\sigma}$, elements $\delta P_{ij\sigma}$ of the response of the density matrix are nonzero [see Eq. 4.7], it is convenient to treat only these elements, and to divide $\delta \boldsymbol{P}$ into particle-hole and hole-particle parts. (Although the "particle", "hole" terminology is not particularly apt in the case of fractional occupation numbers, it remains both unambiguous, with the above definition, and convenient.) Since $\delta \boldsymbol{P}$ is hermitian, the ph and hp parts will be related by complex conjugation. This will lead to a reduction, by a factor of 2, in the dimension of the matrix equations to be solved, as well as facilitate the separation of equations for the real and imaginary parts of $\delta \boldsymbol{P}$, which is useful not only because it allows the computations to be done with real arithmetic when A_{xc}, and thus $\boldsymbol{K}$, is real, but also because often only the real part of $\delta \boldsymbol{P}$ is needed [see e.g. Eq. (4.12)]. This separation of particle and hole parts is also used in TDHF [60].

Start by ordering the orbital basis $\psi_{i\sigma}$ such that $i < j \leftrightarrow f_{i\sigma} \geq f_{j\sigma}$. Now consider only $f_{i\sigma} > f_{j\sigma}$. Then $\delta P_{ij\sigma}$ are ph matrix elements, and $\delta P_{ji\sigma}$ are hp matrix elements, and similarly for δv^{appl}. Note that Eq. (4.11) involves both ph and hp matrix elements. It can be written as two equations, the first giving the ph part of δv^{appl},

$$\sum_{kl\tau}^{f_{k\tau}-f_{l\tau}>0} \left[\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}\frac{\omega - (\epsilon_{k\tau} - \epsilon_{l\tau})}{f_{l\tau} - f_{k\tau}} - K_{ij\sigma,kl\tau}(\omega) \right] \delta P_{kl\tau}(\omega)$$

$$- \sum_{kl\tau}^{f_{k\tau}-f_{l\tau}>0} K_{ij\sigma,lk\tau}(\omega)\delta P_{lk\tau}(\omega) = \delta v^{\mathrm{appl}}_{ij\sigma}(\omega) \qquad (4.19)$$

and the second giving the hp part of δv^{appl},

$$\sum_{kl\tau}^{f_{k\tau}-f_{l\tau}>0} \left[\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}\frac{\omega - (\epsilon_{l\tau} - \epsilon_{k\tau})}{f_{k\tau} - f_{l\tau}} - K_{ji\sigma,lk\tau}(\omega) \right] \delta P_{lk\tau}(\omega)$$

$$- \sum_{kl\tau}^{f_{k\tau}-f_{l\tau}>0} K_{ji\sigma,kl\tau}(\omega)\delta P_{kl\tau}(\omega) = \delta v^{\mathrm{appl}}_{ji\sigma}(\omega) \,. \qquad (4.20)$$

If the MOs are real, then by using the symmetry property (4.14) [or (4.17) in the TDHF case], these two equations can be combined into a single matrix equation,

$$\left\{ \begin{bmatrix} \boldsymbol{\mathcal{A}}(\omega) & \boldsymbol{\mathcal{B}}(\omega) \\ \boldsymbol{\mathcal{B}}(\omega) & \boldsymbol{\mathcal{A}}(\omega) \end{bmatrix} - \omega \begin{bmatrix} \boldsymbol{\mathcal{C}} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{\mathcal{C}} \end{bmatrix} \right\} \begin{bmatrix} \delta\vec{P}(\omega) \\ \delta\vec{P}^*(\omega) \end{bmatrix} = \begin{bmatrix} \delta\vec{v}_{\mathrm{appl}}(\omega) \\ \delta\vec{v}^*_{\mathrm{appl}}(\omega) \end{bmatrix} , \qquad (4.21)$$

where

$$\mathcal{A}_{ij\sigma,kl\tau}(\omega) = \delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}\frac{\epsilon_{k\tau} - \epsilon_{l\tau}}{f_{k\tau} - f_{l\tau}} - K_{ij\sigma,kl\tau}(\omega) \,, \qquad (4.22)$$

$$\mathcal{B}_{ij\sigma,kl\tau}(\omega) = -K_{ij\sigma,lk\tau}(\omega) \,, \qquad (4.23)$$

$$\mathcal{C}_{ij\sigma,kl\tau} = \frac{\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}}{f_{k\tau} - f_{l\tau}} \,, \qquad (4.24)$$

$\delta\vec{P}(\omega)$ denotes the Fourier transform of $\delta\vec{P}(t)$ (so $\delta P_{lk\tau}(\omega) = \delta P^*_{kl\tau}(\omega)$, but note that this does not equal $[\delta P_{kl\tau}(\omega)]^*$), and similarly for $\delta\vec{v}^*_{\mathrm{appl}}(\omega)$. Note that, in each block, the rows

are labeled by $ij\sigma$ with $f_{i\sigma} > f_{j\sigma}$ and the columns are labeled by $kl\tau$ with $f_{k\tau} > f_{l\tau}$. A suitable unitary transformation of Eq. (4.21) gives

$$\left\{ \begin{bmatrix} \mathcal{A}(\omega) + \mathcal{B}(\omega) & 0 \\ 0 & \mathcal{A}(\omega) - \mathcal{B}(\omega) \end{bmatrix} - \omega \begin{bmatrix} 0 & -\mathcal{C} \\ -\mathcal{C} & 0 \end{bmatrix} \right\} \begin{bmatrix} \mathrm{Re}\,\delta\vec{P}(\omega) \\ -i\,\mathrm{Im}\,\delta\vec{P}(\omega) \end{bmatrix}$$
$$= \begin{bmatrix} \mathrm{Re}\,\delta\vec{v}_{\mathrm{appl}}(\omega) \\ -i\,\mathrm{Im}\,\delta\vec{v}_{\mathrm{appl}}(\omega) \end{bmatrix}, \qquad (4.25)$$

which can be used to obtain separate equations for the real and imaginary parts of $\delta\vec{P}$,

$$\left\{ [\mathcal{A}(\omega) + \mathcal{B}(\omega)] - \omega^2 \mathcal{C}\,[\mathcal{A}(\omega) - \mathcal{B}(\omega)]^{-1}\,\mathcal{C} \right\} \left(\mathrm{Re}\,\delta\vec{P} \right)(\omega)$$
$$= \left(\mathrm{Re}\,\delta\vec{v}_{\mathrm{appl}} \right)(\omega) + i\omega\mathcal{C}\,[\mathcal{A}(\omega) - \mathcal{B}(\omega)]^{-1}\,\left(\mathrm{Im}\,\delta\vec{v}_{\mathrm{appl}} \right)(\omega), \qquad (4.26)$$

and

$$\left\{ [\mathcal{A}(\omega) - \mathcal{B}(\omega)] - \omega^2 \mathcal{C}\,[\mathcal{A}(\omega) + \mathcal{B}(\omega)]^{-1}\,\mathcal{C} \right\} \left(\mathrm{Im}\,\delta\vec{P} \right)(\omega)$$
$$= \left(\mathrm{Im}\,\delta\vec{v}_{\mathrm{appl}} \right)(\omega) - i\omega\mathcal{C}\,[\mathcal{A}(\omega) + \mathcal{B}(\omega)]^{-1}\,\left(\mathrm{Re}\,\delta\vec{v}_{\mathrm{appl}} \right)(\omega). \qquad (4.27)$$

These equations are equally valid for the TDHF approximation and for TD-DFRT. However, $[\mathcal{A}(\omega) - \mathcal{B}(\omega)]$ is a diagonal ω-independent matrix in TD-DFRT, but is not diagonal in the TDHF approximation due to the lower symmetry of $\mathbf{K}$ [see Eqs. (4.18) and (4.14)]. Thus computations are considerably simpler in TD-DFRT where, for real perturbations, the real part of the response of the density matrix is given by

$$\sum_{kl\tau}^{f_{k\tau} - f_{l\tau} > 0} \left[\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}\frac{\epsilon_{k\sigma} - \epsilon_{l\sigma}}{f_{k\sigma} - f_{l\sigma}} - 2K_{ij\sigma,kl\tau}(\omega) \right.$$
$$\left. - \omega^2 \frac{\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}}{(f_{k\tau} - f_{l\tau})(\epsilon_{k\tau} - \epsilon_{l\tau})} \right] \left(\mathrm{Re}\,\delta P_{kl\tau} \right)(\omega) = \delta v_{ij\sigma}^{\mathrm{appl}}(\omega). \qquad (4.28)$$

D. Excitation Energies and Oscillator Strengths

The interaction of a molecule with light can be modeled as the interaction with an electric field varying sinusoidally in time. Excitation energies and oscillator strengths can then be obtained from the poles and residues of the dynamic polarizability. Since the perturbation is real in this case, and the polarizability involves only the real part of $\delta\vec{P}$ [see Eq. (4.12)], it suffices to solve Eq. (4.26). The solution can be expressed as

$$\left(\mathrm{Re}\,\delta\vec{P} \right)(\omega) = \mathcal{S}^{-1/2} \left\{ \omega^2 \mathbf{1} - \Omega(\omega) \right\}^{-1} \mathcal{S}^{-1/2} \delta\vec{v}_{\mathrm{appl}}(\omega), \qquad (4.29)$$

where

$$\mathcal{S}(\omega) = -\mathcal{C}\,(\mathcal{A} - \mathcal{B})^{-1}\,\mathcal{C} \qquad (4.30)$$

and

$$\Omega(\omega) = -\mathcal{S}^{-1/2}\,(\mathcal{A} + \mathcal{B})\,\mathcal{S}^{-1/2}. \qquad (4.31)$$

This solution also holds for TDHF, but in TD-DFRT $\mathcal{S}$ and Ω simplify considerably to become

$$\mathcal{S}_{ij\sigma,kl\tau} = \frac{\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}}{(f_{k\tau} - f_{l\tau})(\epsilon_{l\tau} - \epsilon_{k\tau})} > 0\,, \tag{4.32}$$

and

$$\Omega_{ij\sigma,kl\tau}(\omega) = \delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}\left(\epsilon_{l\tau} - \epsilon_{k\tau}\right)^2$$
$$+ 2\sqrt{(f_{i\sigma} - f_{j\sigma})(\epsilon_{j\sigma} - \epsilon_{i\sigma})}K_{ij\sigma,kl\tau}(\omega)\sqrt{(f_{k\tau} - f_{l\tau})(\epsilon_{l\tau} - \epsilon_{k\tau})}\,. \tag{4.33}$$

Combining Eqs. (4.12) and (4.29) gives a formula for the dynamic polarizability,

$$\alpha_{xz}(\omega) = 2\vec{x}^{\dagger}\mathcal{S}^{-1/2}\left\{\Omega(\omega) - \omega^2\mathbf{1}\right\}^{-1}\mathcal{S}^{-1/2}\vec{z}\,. \tag{4.34}$$

The excitation energies and oscillator strengths may be obtained by comparing this with the SOS formula for the polarizability [see Eqs. (3.22) - (3.25)]. Since $\alpha(\omega)$ has poles at the excitation energies, ω_I, it follows that the excitation energies are the solutions of the pseudoeigenvalue problem,

$$\Omega(\omega)\vec{F}_I = \omega_I^2\vec{F}_I\,. \tag{4.35}$$

It is also clear from the SOS formula (3.22) that $\alpha(\omega)$ is an even function of ω, thus $\Omega(\omega)$ and $K(\omega)$ must also be even functions of ω, and hence [Eq. (4.13)] are hermitian matrices.

More information can be extracted from the comparison with the SOS formula by using the spectral expansion,

$$\left\{\Omega(\omega) - \omega^2\mathbf{1}\right\}^{-1} = \sum_I \frac{R_I}{\omega_I^2 - \omega^2}\vec{F}_I\vec{F}_I^{\dagger}\,. \tag{4.36}$$

Note that $R_I \neq 1$ if the pseudoeigenvectors $\vec{F}_I$ are normalized to 1 (unless Ω is independent of ω). Instead, it is convenient to renormalize the $\vec{F}_I$ such that $R_I = 1$. The value of R_I is most easily determined for nondegenerate states, in which case

$$\left\{\Omega(\omega) - \omega^2\mathbf{1}\right\}^{-1} \cong \frac{R_I}{\omega_I^2 - \omega^2}\vec{F}_I\vec{F}_I^{\dagger} \tag{4.37}$$

near $\omega = \omega_I$. Then

$$R_I^{-1} \cong \vec{F}_I^{\dagger}\frac{\omega^2\mathbf{1} - \Omega(\omega)}{\omega^2 - \omega_I^2}\vec{F}_I \rightarrow \vec{F}_I^{\dagger}\left\{\mathbf{1} - \left[\frac{\partial\Omega(\omega)}{\partial\omega^2}\right]_{\omega=\omega_I}\right\}\vec{F}_I \tag{4.38}$$

as $\omega \rightarrow \omega_I$. Renormalizing the pseudoeigenvectors such that

$$\vec{F}_I^{\dagger}\left\{\mathbf{1} - \left[\frac{\partial\Omega(\omega)}{\partial\omega^2}\right]_{\omega=\omega_I}\right\}\vec{F}_I = 1 \tag{4.39}$$

then yields $R_I = 1$. Henceforth $\vec{F}_I$ will always refer to these renormalized pseudoeigenvectors.

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Rewriting Eq. (4.34) using the spectral expansion in terms of the renormalized $\vec{F}_I$, and comparing with the SOS formula (3.22) shows that

$$\vec{x}^\dagger \boldsymbol{S}^{-1/2} \vec{F}_I = \omega_I^{1/2} \langle \Psi_0 | \hat{x} | \Psi_I \rangle \tag{4.40}$$

so that the oscillator strengths are just given by

$$f_I = \frac{2}{3} \left(\left| \vec{x}^\dagger \boldsymbol{S}^{-1/2} \vec{F}_I \right|^2 + \left| \vec{y}^\dagger \boldsymbol{S}^{-1/2} \vec{F}_I \right|^2 + \left| \vec{z}^\dagger \boldsymbol{S}^{-1/2} \vec{F}_I \right|^2 \right) . \tag{4.41}$$

According to the Thomas–Reiche–Kuhn (TRK) sum rule [61], the sum of the oscillator strengths should equal the number of electrons. This can be used to guage the quality of the basis set, when working with frequency-independent approximations for $\boldsymbol{K}$. When $\boldsymbol{\Omega}$ is independent of ω, the renormalized $\vec{F}_I$ form a complete orthonormal set,

$$\sum_I \vec{F}_I \vec{F}_I^\dagger = \boldsymbol{1} . \tag{4.42}$$

It then follows that

$$\sum_I f_I = \frac{2}{3} \left(\vec{x}^\dagger \boldsymbol{S}^{-1} \vec{x} + \vec{y}^\dagger \boldsymbol{S}^{-1} \vec{y} + \vec{z}^\dagger \boldsymbol{S}^{-1} \vec{z} \right) , \tag{4.43}$$

independent of how the coupling matrix is approximated as long as it is frequency independent. Since the TRK sum rule applies to a system of independent particles, the expression (4.43) must converge to the number of electrons, in the limit of a complete basis set, for any frequency-independent $\boldsymbol{K}$.

E. The assignment problem

Having calculated the excitation energies, ω_I, and oscillator strengths, f_I, it remains to assign the states Ψ_I. Up to this point, no assumption has been made as to the form of the ground or excited state wavefunctions. However, for purposes of making assignments, it is convenient, if not strictly necessary, to make some approximations. The first of these is that Ψ_0 is a single determinant, Φ, of Kohn–Sham orbitals. (This assumption should be appropriately modified for open shell systems.) Equation (4.40) can then be rewritten as

$$\sum_{ij\sigma}^{f_{i\sigma}-f_{j\sigma}>0} x_{ij\sigma} \left(\boldsymbol{S}^{-1/2} \vec{F}_I \right)_{ij\sigma} = \omega_I^{1/2} \sum_{ij\sigma}^{f_{i\sigma}-f_{j\sigma}>0} x_{ij\sigma} \langle \Phi | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_I \rangle . \tag{4.44}$$

The second assumption is that the

$$x_{ij\sigma} = \int \psi_{i\sigma}(\mathbf{r}) \hat{x} \psi_{j\sigma}(\mathbf{r}) \, d\mathbf{r} \tag{4.45}$$

are linearly independent so that

$$\omega_I^{1/2} \langle \Phi | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_I \rangle = \left(\boldsymbol{S}^{-1/2} \vec{F}_I \right)_{ij\sigma}$$
$$= \sqrt{(f_{i\sigma} - f_{j\sigma})(\epsilon_{j\sigma} - \epsilon_{i\sigma})} F_{ij\sigma}^I . \tag{4.46}$$

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This would have been obtained without any assumptions in a theory encompassing non-local external potentials and the response of the true density matrix. However, strictly speaking, DFT is limited to densities and local external potentials. As a result, Eq. (4.46) requires the assumption of linear independence of the $x_{ij\sigma}$, or, more precisely, of the products $\psi_{i\sigma}(\mathbf{r})\psi_{j\sigma}(\mathbf{r})$ appearing in the calculation of the matrix elements of local operators. This is probably reasonable when the MO basis is not too large, but linear dependencies among the products $\{\psi_{i\sigma}(\mathbf{r})\psi_{j\sigma}(\mathbf{r})\}$ become likely as the MO basis approaches completion [62]. Nevertheless, Eq. (4.46) fixes the coefficients

$$c_{ij\sigma}^I = \sqrt{\frac{\epsilon_{j\sigma} - \epsilon_{i\sigma}}{\omega_I}} F_{ij\sigma}^I \tag{4.47}$$

of the singly excited configurations in the expansion

$$\Psi_I = \sum_{ij\sigma}^{f_{i\sigma} - f_{j\sigma} > 0} c_{ij\sigma}^I \hat{a}_{j\sigma}^\dagger \hat{a}_{i\sigma} \Phi + \cdots \tag{4.48}$$

which is adequate for making a qualitative assignment. Notice that multideterminantal excited states have arisen from solutions of the pseudoeigenvalue problem (4.35). Naturally, this assignment method could be made more rigorous by using a better expression for Ψ_0 and by taking linear dependencies between MO product functions explicitly into account. However we have not yet found this to be necessary in making qualitative assignments for simple closed shell systems.

V. Auxiliary-function method

One of the important advantages of DFT is that it involves only local potentials and thus is less computationally demanding than other *ab initio* methods. Part of the advantage of the locality of v_{xc} comes from additional symmetry, which is reflected, for example, in the TD-DFRT coupling matrix (in the adiabatic approximation), as opposed to the TDHF coupling matrix [see Eqs. (4.14) and (4.18)], and considerably simplifies the construction of $\mathbf{\Omega}$. Another advantage of the locality of v_{xc} is that it lends itself readily to an auxiliary function method which allows the costly four-center integrals to be eliminated [63,64]. Since practical auxiliary basis sets are incomplete, this gain in computational efficiency does entail some reduction in accuracy. This generally shows up primarily as a systematic shift in absolute energies, which does not have a large effect on most properties of practical interest since these usually involve energy differences. Not all DFT programs use an auxiliary function approach, notably the DFT options implemented in HF programs such as GAUSSIAN [65] and CADPAC [66], evaluate four-center integrals. However, the approach adopted here is to capitalize on the computational advantages of DFT by using auxiliary functions, as is done in DFT programs such as deMon (for *densité de Montréal*) [67–69] and DGauss [70]. From the practical point of view of the implementation and testing of TD-DFRT as a post-deMon program, this has the additional advantage that the static polarizabilities thus obtained should be the same as those obtained from deMon using the finite-field method (within the numerical error of the latter).

In the static limit, the TD-DFRT equations, in the adiabatic approximation, reduce to the coupled perturbed DFT equations. An auxiliary function treatment of the coupled perturbed DFT equations appropriate for implementation in deMon has been given by Fournier [19], in the context of calculating analytic second derivatives of potential energy surfaces.

The present section first reviews the auxiliary function method used in deMon, and then shows how this can be used to eliminate the four-center integrals in the coupling matrix.

Two different auxiliary basis sets are used in deMon, one for handling the coulomb potential and the other for the exchange-correlation potential. Consider first the coulomb potential. Its matrix elements, in the atomic orbital basis set $\{\chi_\mu\}$, are given by

$$(v_{\text{coul}})^\sigma_{\mu,\nu} = [\chi_\mu \chi_\nu^* | \rho] \,, \tag{5.1}$$

in terms of the inner product defined in Eq. (4.10). Expanding the density in the same basis set [cf. Eq. (4.4)],

$$\rho_\sigma(\mathbf{r}) = \sum_{\mu,\nu} \chi_\mu(\mathbf{r}) \chi_\nu^*(\mathbf{r}) P_{\mu\nu\sigma} \,, \tag{5.2}$$

results in an expression for the coulomb matrix elements involving integrals over four centers. These integrals are avoided in deMon by expanding the charge density in an auxiliary basis set of atom-centered Gaussian-type orbitals, g_I^{cd},

$$\tilde{\rho}(\mathbf{r}) = \sum_I g_I^{\text{cd}}(\mathbf{r}) a_I \,, \tag{5.3}$$

where the tilde has been added to emphasize that this expansion may differ from the charge density, ρ, since, in practice, the auxiliary basis is incomplete. The fitting coefficients, a_I, are normally determined by minimizing $[\rho - \tilde{\rho} | \rho - \tilde{\rho}]$ subject to the constraint,

$$\int \tilde{\rho}(\mathbf{r}) \, d\mathbf{r} = N \,. \tag{5.4}$$

However, note that this constraint is automatically satisfied when $\tilde{\rho} \to \rho$. Our tests do not show significant differences in the polarizabilities calculated with or without this constraint, with the auxiliary basis sets we normally use [71]. Minimizing $[\rho - \tilde{\rho} | \rho - \tilde{\rho}]$ without the normalization constraint gives

$$a_I = \sum_J \left(S^{\text{cd}}\right)^{-1}_{I,J} [g_J^{\text{cd}} | \rho] \,, \tag{5.5}$$

where the overlap matrix

$$S_{I,J}^{\text{cd}} = [g_I^{\text{cd}} | g_J^{\text{cd}}] \,. \tag{5.6}$$

Thus the matrix elements of the coulomb potential become

$$v_{\mu\nu\sigma}^{\text{coul}} = \sum_{IJ} [\chi_\mu \chi_\nu^* | g_I^{\text{cd}}] \left(S^{\text{cd}}\right)^{-1}_{I,J} \sum_{\mu',\nu',\sigma'} [g_J^{\text{cd}} | \chi_{\mu'} \chi_{\nu'}^*] P_{\mu'\nu'\sigma'} \,. \tag{5.7}$$

Of course this is equivalent to

$$v_{\mu\nu\sigma}^{\text{coul}} = \sum_{\mu',\nu',\sigma'} [\chi_\mu \chi_\nu^* | \chi_{\mu'} \chi_{\nu'}^*] P_{\mu'\nu'\sigma'} \tag{5.8}$$

in the limit of a complete auxiliary basis set.

Now consider the exchange-correlation potential, whose matrix elements are

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$$v_{\mu\nu\sigma}^{\mathrm{xc}} = \int \chi_\mu^*(\mathbf{r}) v_{\mathrm{xc}}^\sigma[\rho_\uparrow, \rho_\downarrow](\mathbf{r}) \chi_\nu(\mathbf{r}) \, d\mathbf{r} \, . \tag{5.9}$$

Since it is generally not possible to evaluate these integrals analytically, v_{xc} in Eq. (5.9) is expanded in an auxiliary basis set of atom-centered Gaussian-type orbitals, g_I^{xc},

$$\tilde{v}_{\mathrm{xc}}^\sigma(\mathbf{r}) = \sum_I g_I^{\mathrm{xc}}(\mathbf{r}) b_I^\sigma \, , \tag{5.10}$$

where, again, the tilde serves to emphasize that this expansion is, in practice, an approximation to v_{xc}^σ. The fitting coefficients are determined by minimizing $\{v_{\mathrm{xc}} - \tilde{v}_{\mathrm{xc}} | v_{\mathrm{xc}} - \tilde{v}_{\mathrm{xc}}\}$, where the inner product

$$\{f|g\} = \sum_i^{\mathrm{grid}} w_i f^*(\mathbf{r}_i) g(\mathbf{r}_i) \tag{5.11}$$

approximates $\langle f|g \rangle$ by quadrature with grid points, $\mathbf{r}_i$, and weights, w_i. (Note, however, that the number of grid points required for this fit is much smaller than the number that would be needed to do the integral (5.9) numerically.) The minimization results in

$$b_I^\sigma = \sum_J (S^{\mathrm{xc}})_{I,J}^{-1} \{g_J^{\mathrm{xc}}|v_{\mathrm{xc}}^\sigma\} \, , \tag{5.12}$$

where the overlap matrix,

$$S_{I,J}^{\mathrm{xc}} = \{g_I^{\mathrm{xc}}|g_J^{\mathrm{xc}}\} \, . \tag{5.13}$$

Thus the matrix elements of the exchange-correlation potential become

$$v_{\mu\nu\sigma}^{\mathrm{xc}} = \sum_{I,J} \langle \chi_\mu|g_I^{\mathrm{xc}}|\chi_\nu\rangle \, (S^{\mathrm{xc}})_{I,J}^{-1} \{g_J^{\mathrm{xc}}|v_{\mathrm{xc}}^\sigma\} \, . \tag{5.14}$$

These auxiliary function expressions for the coulomb and exchange-correlation matrix elements can now be used to write down auxiliary function expressions for the matrix elements of the coupling matrix, that do not involve four-center integrals. The adiabatic approximation is assumed in this section, so the coupling matrix is the same as for the static case. The coupling matrix (4.9) is the sum of a coulomb term and an exchange-correlation term,

$$K_{\mu\nu\sigma,\mu'\nu'\sigma'} = K_{\mu\nu\sigma,\mu'\nu'\sigma'}^{\mathrm{coul}} + K_{\mu\nu\sigma,\mu'\nu'\sigma'}^{\mathrm{xc}} = \frac{\partial v_{\mu\nu\sigma}^{\mathrm{coul}}}{\partial P_{\mu'\nu'\sigma'}} + \frac{\partial v_{\mu\nu\sigma}^{\mathrm{xc}}}{\partial P_{\mu'\nu'\sigma'}} \, . \tag{5.15}$$

Hence, using Eq. (5.7) for $v_{\mu\nu\sigma}^{\mathrm{coul}}$,

$$K_{\mu\nu\sigma,\mu'\nu'\sigma'}^{\mathrm{coul}} = \sum_{IJ} [\chi_\mu \chi_\nu^*|g_I^{\mathrm{cd}}] \left(S^{\mathrm{cd}}\right)_{I,J}^{-1} \sum_{\mu',\nu'} [g_J^{\mathrm{cd}}|\chi_{\mu'} \chi_{\nu'}^*] \, . \tag{5.16}$$

Of course this is equivalent to

$$K_{\mu\nu\sigma,\mu'\nu'\sigma'}^{\mathrm{coul}} = [\chi_\mu \chi_\nu^*|\chi_{\mu'} \chi_{\nu'}^*] \tag{5.17}$$

in the limit of a complete auxiliary basis set. Similarly, using Eq. (5.14) for $v_{\mu\nu\sigma}^{\mathrm{xc}}$ and taking the derivative gives

$$K^{\mathrm{xc}}_{\mu\nu\sigma,\mu'\nu'\sigma'} = \sum_{I,J} \langle \chi_\mu | g^{\mathrm{xc}}_I | \chi_\nu \rangle \, (S^{\mathrm{xc}})^{-1}_{I,J} \, \{ g^{\mathrm{xc}}_J | \int \frac{\delta v^\sigma_{\mathrm{xc}}}{\delta \rho_{\sigma'}(\mathbf{r})} \frac{\partial \rho_{\sigma'}(\mathbf{r})}{\partial P_{\mu'\nu'\sigma'}} \, d\mathbf{r} \} \tag{5.18}$$

or, using Eq. (5.2),

$$K^{\mathrm{xc}}_{\mu\nu\sigma,\mu'\nu'\sigma'} = \sum_{I,J} \langle \chi_\mu | g^{\mathrm{xc}}_I | \chi_\nu \rangle \, (S^{\mathrm{xc}})^{-1}_{I,J} \, \{ g^{\mathrm{xc}}_J | \int \frac{\delta v^\sigma_{\mathrm{xc}}}{\delta \rho_{\sigma'}(\mathbf{r})} \chi_{\mu'}(\mathbf{r}) \chi^*_{\nu'}(\mathbf{r}) \, d\mathbf{r} \} \,. \tag{5.19}$$

The integral shown in Eq. (5.19) is difficult to evaluate except in the local density approximation (LDA) where it is trivial,

$$\int \frac{\delta v^\sigma_{\mathrm{xc}}(\mathbf{r})}{\delta \rho_{\sigma'}(\mathbf{r}')} \chi_\mu(\mathbf{r}') \chi^*_\nu(\mathbf{r}') \, d\mathbf{r}' = \frac{\delta v^\sigma_{\mathrm{xc}}(\mathbf{r})}{\delta \rho_{\sigma'}(\mathbf{r})} \chi_\mu(\mathbf{r}) \chi^*_\nu(\mathbf{r}) \,. \tag{5.20}$$

Hence

$$K^{\mathrm{xc}}_{\mu\nu\sigma,\mu'\nu'\sigma'} = \sum_{I,J} \langle \chi_\mu | g^{\mathrm{xc}}_I | \chi_\nu \rangle \, (S^{\mathrm{xc}})^{-1}_{I,J} \, \{ g^{\mathrm{xc}}_J | \frac{\delta v^\sigma_{\mathrm{xc}}}{\delta \rho_{\sigma'}} | \chi_{\mu'} \chi^*_{\nu'} \} \,, \tag{5.21}$$

in an obvious extension of the notation. Since small errors in the quadrature scheme can result in loss of hermitivity, $\boldsymbol{K}^{\mathrm{xc}}$ is symmetrized before solving the excitation eigenvalue problem (4.34).

VI. H_2 as an illustrative example

The TD-DFRT treatment of section IV is illustrated here for the simple textbook example of H_2 described by a minimal basis set. The resulting excitation energy and oscillator strength expressions are compared with those obtained from HF, and from the usual ΔSCF-based DFT approach.

The treatment is spin-restricted and the minimal basis set consists of an s-orbital on each center. The molecular orbitals are completely determined by symmetry to be the σ-bonding combination,

$$\psi_g(\mathbf{r}) = \frac{s_A(\mathbf{r}) + s_B(\mathbf{r})}{\sqrt{2(1 + \langle s_A | s_B \rangle)}} \,, \tag{6.1}$$

and the σ-antibonding combination,

$$\psi_u(\mathbf{r}) = \frac{s_A(\mathbf{r}) - s_B(\mathbf{r})}{\sqrt{2(1 - \langle s_A | s_B \rangle)}} \,, \tag{6.2}$$

so there is no degree of freedom to describe relaxation on excitation. The ground state of H_2 is a singlet given by the single determinant

$$\Phi = |\psi_g \bar{\psi}_g| \,, \tag{6.3}$$

where ψ_g and $\bar{\psi}_g$ refer to the spin-up and spin-down spin orbitals, respectively. There is one singlet excited state,

$$\Phi^1_0 = \frac{1}{\sqrt{2}} (|\psi_g \bar{\psi}_u| + |\psi_u \bar{\psi}_g|) \,, \tag{6.4}$$

and, neglecting all spin-couplings, three degenerate triplet excited states,

$$\Phi_1^3 = |\psi_g \psi_u| \,, \tag{6.5}$$

$$\Phi_0^3 = \frac{1}{\sqrt{2}}(|\psi_g \bar{\psi}_u| - |\psi_u \bar{\psi}_g|) \,, \tag{6.6}$$

$$\Phi_{-1}^3 = |\bar{\psi}_g \bar{\psi}_u| \,. \tag{6.7}$$

According to Eqs. (4.33) and (4.35), the excitation energies are obtained by solving the eigenvalue problem

$$\left[\begin{array}{cc} (\epsilon_u - \epsilon_g)^2 + 2(\epsilon_u - \epsilon_g)K_{\uparrow,\uparrow} & 2(\epsilon_u - \epsilon_g)K_{\uparrow,\downarrow} \\ 2(\epsilon_u - \epsilon_g)K_{\downarrow,\uparrow} & (\epsilon_u - \epsilon_g)^2 + 2(\epsilon_u - \epsilon_g)K_{\downarrow,\downarrow} \end{array} \right] \vec{F}_I = \omega_I^2 \vec{F}_I \,, \tag{6.8}$$

where

$$K_{\sigma,\tau} = [\psi_g \psi_u | \psi_g \psi_u] + \int\!\!\int \psi_g(\mathbf{r})\psi_u(\mathbf{r}) \frac{\delta v_{\text{xc}}^{\sigma}(\mathbf{r})}{\delta \rho_\tau(\mathbf{r}')} \psi_g(\mathbf{r}')\psi_u(\mathbf{r}') \, d\mathbf{r} d\mathbf{r}' \,, \tag{6.9}$$

in the adiabatic approximation. Equation (6.8) has two solutions, one with

$$\vec{F}_T = \frac{1}{\sqrt{2}} \left[\begin{array}{c} 1 \\ -1 \end{array} \right] \,, \tag{6.10}$$

$$\begin{aligned} \omega_T &= \sqrt{(\epsilon_u - \epsilon_g)[(\epsilon_u - \epsilon_g) + 2(K_{\uparrow,\uparrow} - K_{\uparrow,\downarrow})]} \\ &\cong \epsilon_u - \epsilon_g + K_{\uparrow,\uparrow} - K_{\uparrow,\downarrow} \\ &= \epsilon_u - \epsilon_g + \int\!\!\int \psi_g(\mathbf{r})\psi_u(\mathbf{r}) \left[\frac{\delta v_{\text{xc}}^{\uparrow}(\mathbf{r})}{\delta \rho_\uparrow(\mathbf{r}')} - \frac{\delta v_{\text{xc}}^{\uparrow}(\mathbf{r})}{\delta \rho_\downarrow(\mathbf{r}')} \right] \psi_g(\mathbf{r}')\psi_u(\mathbf{r}') \, d\mathbf{r} d\mathbf{r}' \,, \end{aligned} \tag{6.11}$$

corresponding to the transition to the triplet excited state Φ_0^3, and the other,

$$\vec{F}_S = \frac{1}{\sqrt{2}} \left[\begin{array}{c} 1 \\ 1 \end{array} \right] \,, \tag{6.12}$$

$$\begin{aligned} \omega_S &= \sqrt{(\epsilon_u - \epsilon_g)[(\epsilon_u - \epsilon_g) + 2(K_{\uparrow,\uparrow} + K_{\uparrow,\downarrow})]} \\ &\cong \epsilon_u - \epsilon_g + K_{\uparrow,\uparrow} + K_{\uparrow,\downarrow} \\ &= \epsilon_u - \epsilon_g + 2[\psi_g \psi_u | \psi_g \psi_u] + \int\!\!\int \psi_g(\mathbf{r})\psi_u(\mathbf{r}) \left[\frac{\delta v_{\text{xc}}^{\uparrow}(\mathbf{r})}{\delta \rho_\uparrow(\mathbf{r}')} + \frac{\delta v_{\text{xc}}^{\uparrow}(\mathbf{r})}{\delta \rho_\downarrow(\mathbf{r}')} \right] \psi_g(\mathbf{r}')\psi_u(\mathbf{r}') \, d\mathbf{r} d\mathbf{r}' \,, \end{aligned} \tag{6.13}$$

corresponding to the transition to the singlet excited state Φ_0^1. Note that, since all spin-coupling has been ignored, the response theory yields only one of the triplet states, namely Φ_0^3, which results from the transition that conserves the spin azimuthal quantum number M_S. However, inclusion of interactions that break the degeneracy of the triplet would result in the response theory producing all three states. In the present case, only the singlet-singlet transition has a nonzero oscillator strength [Eq. (4.41)],

$$f_S = \frac{4}{3}(\epsilon_u - \epsilon_g) \left(|\langle \psi_g | \hat{x} | \psi_u \rangle|^2 + |\langle \psi_g | \hat{y} | \psi_u \rangle|^2 + |\langle \psi_g | \hat{z} | \psi_u \rangle|^2 \right) \,. \tag{6.14}$$

The mean dynamic polarizability [Eq. (3.25) or (4.34)] is simply

$$\bar{\alpha}(\omega) = \frac{f_S}{\omega_S^2 - \omega^2} \, . \tag{6.15}$$

In order to go beyond the adiabatic approximation, the derivative $\delta v_{\text{xc}}^{\sigma}(\mathbf{r})/\delta\rho_\tau(\mathbf{r}')$ in Eq. (6.9) would be replaced by the Fourier transform of $\delta A_{\text{xc}}/\delta\rho_\sigma(\mathbf{r},t)\delta\rho_\tau(\mathbf{r}',t')$ and $\boldsymbol{K}$ would become ω-dependent. In the present simple example this would change the excitation energies, and would modify the $\vec{F}_I$, and thus the oscillator strengths, through the renormalization (4.39).

As was noted in Sec. IV B, the TDHF coupling matrix is obtained in exactly the same manner as the TD-DFRT coupling matrix, except that the derivative of the exchange-correlation term in TD-DFRT is replaced by the derivative of the exchange operator in TDHF. Thus the (ph,ph)-part of the TD-DFRT coupling matrix becomes the (ph,ph)-part of the TDHF coupling matrix, if the replacement

$$\iint \psi_g(\mathbf{r})\psi_u(\mathbf{r})\frac{\delta v_{\text{xc}}^{\sigma}(\mathbf{r})}{\delta\rho_\tau(\mathbf{r}')}\psi_g(\mathbf{r}')\psi_u(\mathbf{r}')\,d\mathbf{r}d\mathbf{r}' \to -\delta_{\sigma,\tau}[\psi_g\psi_g|\psi_u\psi_u] \tag{6.16}$$

is made, and the orbital energies are replaced by the corresponding HF orbital energies (the MOs are completely determined by symmetry in the present example). While it may at first be surprising that the derivative of an exchange-correlation term in TD-DFRT corresponds to a coulomb, not an exchange, integral in TDHF, the spin-dependent Kronecker delta before the coulomb integral betrays the fact that this term arises in TDHF as the derivative of an exchange term. Due to the lower symmetry of the TDHF coupling matrix [compare Eq. (4.18) and (4.14)], the TDHF $\boldsymbol{S}$ and $\boldsymbol{\Omega}$ do not have the same direct correspondence with their TD-DFRT counterparts as does the (ph,ph)-part of $\boldsymbol{K}$. In the present example, the $\vec{F}_I$ remain unchanged, but the TDHF excitation energies are given by

$$
\begin{aligned}
\omega_T^{\text{HF}} &= \sqrt{(\epsilon_u - \epsilon_g + K_{\uparrow,\uparrow})(\epsilon_u - \epsilon_g + K_{\uparrow,\uparrow} - 2K_{\uparrow,\downarrow})} \\
&\cong \epsilon_u - \epsilon_g + K_{\uparrow,\uparrow} - K_{\uparrow,\downarrow} \\
&= \epsilon_u - \epsilon_g - [\psi_g\psi_g|\psi_u\psi_u] \\
&= \langle\Phi_0^3|\hat{H}|\Phi_0^3\rangle - \langle\Phi|\hat{H}|\Phi\rangle \, ,
\end{aligned} \tag{6.17}
$$

and

$$
\begin{aligned}
\omega_S^{\text{HF}} &= \sqrt{(\epsilon_u - \epsilon_g + K_{\uparrow,\uparrow})(\epsilon_u - \epsilon_g + K_{\uparrow,\uparrow} + 2K_{\uparrow,\downarrow})} \\
&\cong \epsilon_u - \epsilon_g + K_{\uparrow,\uparrow} + K_{\uparrow,\downarrow} \\
&= \epsilon_u - \epsilon_g + 2[\psi_g\psi_u|\psi_g\psi_u] - [\psi_g\psi_g|\psi_u\psi_u] \\
&= \langle\Phi_0^1|\hat{H}|\Phi_0^1\rangle - \langle\Phi|\hat{H}|\Phi\rangle \, ,
\end{aligned} \tag{6.18}
$$

with the oscillator strength [Eq. (4.41)]

$$f_S^{\text{TDHF}} = \frac{4}{3}(\epsilon_u - \epsilon_g + K_{\uparrow,\uparrow})\left(|\langle\psi_g|\hat{x}|\psi_u\rangle|^2 + |\langle\psi_g|\hat{y}|\psi_u\rangle|^2 + |\langle\psi_g|\hat{z}|\psi_u\rangle|^2\right) \, . \tag{6.19}$$

Note that although the exact expressions for the TDHF excitation energies in terms of the coupling matrix elements differ from the corresponding TD-DFRT expressions by terms of second order in $K_{\sigma,\tau}$ [compare the first lines of Eqs. (6.17) and (6.18) with those of (6.11) and (6.13)], the first-order approximations [second lines of the same equations] do correspond. Note also that the first-order approximation to the TDHF ω_I is just the familiar result

obtained by ignoring orbital relaxation and taking energy differences of HF wavefunction expressions (see e.g. Ref. [72]). Since the MOs are fixed by symmetry in the present example, no relaxation can occur, so this energy difference is the same as the HF ΔSCF excitation energy. This is not the same as the exact TDHF ω_I since TDHF includes a contribution to the excitation energy due to coupling between the HF ground state and doubly-excited configurations [60]. The ΔSCF HF oscillator strengths are obtained from Eq. (3.23), which gives

$$f_S^{\text{HF }\Delta\text{SCF}} = \frac{4}{3}(\epsilon_u - \epsilon_g + K_{\uparrow,\uparrow} + K_{\uparrow,\downarrow}) \left(|\langle\psi_g|\hat{x}|\psi_u\rangle|^2 + |\langle\psi_g|\hat{y}|\psi_u\rangle|^2 + |\langle\psi_g|\hat{z}|\psi_u\rangle|^2 \right) . \quad (6.20)$$

Note that this differs from the TDHF oscillator strength by a small exchange integral term. This is simply a manifestation of the fact that oscillator strengths and excitation energies are not automatically treated to the same level of approximation [73].

The approximate equality of the TDHF and ΔSCF HF excitation energies raises the question as to whether the same might also be true of the TD-DFRT excitation energies and those obtained from the usual ΔSCF-based DFT approach. This is, in fact, not the case, as will now be shown. Rather, coulomb repulsion and exchange-correlation contributions enter differently in the TD-DFRT and ΔSCF-based DFT approaches to excited states.

Although a ΔSCF-based approach is difficult to justify in DFT, except perhaps, for the lowest state of a given symmetry (see Ref. [1] pp. 204-205), it has been the *de facto* DFT treatment of excitation energies. This approach consists of a ΔSCF procedure in which the energy difference is taken between two SCF calculations — one with the ground state electron configuration and one with the excited state electron configuration. Then a correction has to be made to deal with the fact that a simple ΔSCF procedure fails to distinguish between spin and spatial multiplets which have the same density. This is the case for the present example because both the Φ_0^1 and Φ_0^3 wave functions have the same density,

$$\rho_\sigma(\mathbf{r}) = \frac{1}{2} \left(|\psi_g(\mathbf{r})|^2 + |\psi_u(\mathbf{r})|^2 \right) . \quad (6.21)$$

The usual *ad hoc* solution [2,3] to the multiplet problem is to assume that the SCF procedure is only applicable to cases where the excited state is well described by a single determinant wave function, such as for the Φ_1^3 and Φ_{-1}^3 states. The energies of the Φ_0^3 and Φ_0^1 states can then be calculated from the relations

$$E[\Phi_0^3] = E[|\psi_g\psi_u|] \quad (6.22)$$

and

$$E[\Phi_0^1] = 2E[|\psi_g\bar{\psi}_u|] - E[\Phi_0^3] , \quad (6.23)$$

by replacing the energies

$$E[\Psi] = \langle\Psi|\hat{H}|\Psi\rangle , \quad (6.24)$$

corresponding to single determinant wave functions, with the energies obtained from the corresponding DFT SCF calculations. Note that this approach involves using energies from DFT calculations on artificially specified single determinants, such as $|\psi_g\bar{\psi}_u|$, which have no physical existence as eigenstates of the system.

It is convenient for present purposes to estimate ΔSCF excitation energies with the help of the transition state method [6]. This is also sometimes done in practical calculations, in

order to avoid or reduce some of the well-known problems (convergence difficulties, symmetry breaking) encountered in excited state DFT calculations. The transition state method consists of estimating the energy required to excite an electron from the orbital ψ_g with spin σ to the orbital ψ_u with spin τ, by doing an SCF calculation for a transition state with half an electron excited. The ΔSCF excitation energy is approximated as the energy difference between the two half-occupied orbitals. Keeping in mind that no orbital relaxation can occur in the present simple example, and expanding the exchange-correlation potential of the transition state to first-order in the change in the charge density then leads to

$$
\begin{aligned}
E[|\psi_g \psi_u|] - E[|\psi_g \bar{\psi}_g|] \cong{} & \epsilon_u - \epsilon_g - \iint |\psi_g(\mathbf{r})|^2 \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\downarrow(\mathbf{r}')} |\psi_u(\mathbf{r}')|^2 \, d\mathbf{r} d\mathbf{r}' - [\psi_g \psi_g | \psi_u \psi_u] \\
& + \frac{1}{2} \left\{ [\psi_g \psi_g | \psi_g \psi_g] + \iint |\psi_g(\mathbf{r})|^2 \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\uparrow(\mathbf{r}')} |\psi_g(\mathbf{r}')|^2 \, d\mathbf{r} d\mathbf{r}' \right\} \\
& + \frac{1}{2} \left\{ [\psi_u \psi_u | \psi_u \psi_u] + \iint |\psi_u(\mathbf{r})|^2 \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\uparrow(\mathbf{r}')} |\psi_u(\mathbf{r}')|^2 \, d\mathbf{r} d\mathbf{r}' \right\} \quad (6.25)
\end{aligned}
$$

and

$$
\begin{aligned}
E[|\psi_g \bar{\psi}_u|] - E[|\psi_g \bar{\psi}_g|] \cong{} & \epsilon_u - \epsilon_g - \iint |\psi_g(\mathbf{r})|^2 \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\uparrow(\mathbf{r}')} |\psi_u(\mathbf{r}')|^2 \, d\mathbf{r} d\mathbf{r}' - [\psi_g \psi_g | \psi_u \psi_u] \\
& + \frac{1}{2} \left\{ [\psi_g \psi_g | \psi_g \psi_g] + \iint |\psi_g(\mathbf{r})|^2 \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\uparrow(\mathbf{r}')} |\psi_g(\mathbf{r}')|^2 \, d\mathbf{r} d\mathbf{r}' \right\} \\
& + \frac{1}{2} \left\{ [\psi_u \psi_u | \psi_u \psi_u] + \iint |\psi_u(\mathbf{r})|^2 \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\uparrow(\mathbf{r}')} |\psi_u(\mathbf{r}')|^2 \, d\mathbf{r} d\mathbf{r}' \right\} . \quad (6.26)
\end{aligned}
$$

In the analogous HF equations, the terms corresponding to those in the curly brackets in Eqs. (6.25) and (6.26) vanish due to a cancelation of self-interaction errors in the coulomb and exchange energies. To the extent that these terms can also be neglected in the corresponding DFT equations, the singlet-triplet and singlet-singlet excitation energies are then given by,

$$
\omega_T^{\mathrm{DFT}\ \Delta\mathrm{SCF}} \cong \epsilon_u - \epsilon_g - \iint |\psi_g(\mathbf{r})|^2 \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\downarrow(\mathbf{r}')} |\psi_u(\mathbf{r}')|^2 \, d\mathbf{r} d\mathbf{r}' - [\psi_g \psi_g | \psi_u \psi_u] , \quad (6.27)
$$

and

$$
\omega_S^{\mathrm{DFT}\ \Delta\mathrm{SCF}} \cong \epsilon_u - \epsilon_g - \iint |\psi_g(\mathbf{r})|^2 \left[2 \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\uparrow(\mathbf{r}')} - \frac{\delta v_{\mathrm{xc}}^\uparrow(\mathbf{r})}{\delta \rho_\downarrow(\mathbf{r}')} \right] |\psi_u(\mathbf{r}')|^2 \, d\mathbf{r} d\mathbf{r}' - [\psi_g \psi_g | \psi_u \psi_u] .
$$

$$
(6.28)
$$

In non-DFT ΔSCF treatments, oscillator strengths are obtained as the product of the excitation energy and the transition moment [Eq. (3.23)]. The problem in DFT is of course that this calculation of the transition moment requires the N-electron wave functions. Nevertheless, approximate oscillator strengths could be obtained in the ΔSCF-based DFT approach by approximating the wave function by appropriate symmetry-dictated combinations of determinants of Kohn–Sham orbitals [4]. In the present example this is straightforward since the MOs are completely determined by symmetry, and gives

TABLE I. Summary of approximate excitation energy and oscillator strength expressions for H_2

	Excitation energies
	ω_T
TD-DFRT	$\epsilon_u^{\mathrm{KS}} - \epsilon_g^{\mathrm{KS}} + \iint \psi_g(\mathbf{r})\psi_u(\mathbf{r}) \left[\frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\uparrow(\mathbf{r}')} - \frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\downarrow(\mathbf{r}')} \right] \psi_g(\mathbf{r}')\psi_u(\mathbf{r}')\, d\mathbf{r}d\mathbf{r}'$
ΔSCF-based DFT	$\epsilon_u^{\mathrm{KS}} - \epsilon_g^{\mathrm{KS}} - \iint |\psi_g(\mathbf{r})|^2 \frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\downarrow(\mathbf{r}')} |\psi_u(\mathbf{r}')|^2\, d\mathbf{r}d\mathbf{r}' - [\psi_g\psi_g|\psi_u\psi_u] + \mathrm{SIT}^{\mathrm{a}}$
TDHF and ΔSCF HF	$\epsilon_u^{\mathrm{HF}} - \epsilon_g^{\mathrm{HF}} - [\psi_g\psi_g|\psi_u\psi_u]$
	ω_S
TD-DFRT	$\epsilon_u^{\mathrm{KS}} - \epsilon_g^{\mathrm{KS}} + 2[\psi_g\psi_u|\psi_g\psi_u] + \iint \psi_g(\mathbf{r})\psi_u(\mathbf{r}) \left[\frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\uparrow(\mathbf{r}')} + \frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\downarrow(\mathbf{r}')} \right] \psi_g(\mathbf{r}')\psi_u(\mathbf{r}')\, d\mathbf{r}d\mathbf{r}'$
ΔSCF-based DFT	$\epsilon_u^{\mathrm{KS}} - \epsilon_g^{\mathrm{KS}} - \iint |\psi_g(\mathbf{r})|^2 \left[2\frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\uparrow(\mathbf{r}')} - \frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\downarrow(\mathbf{r}')} \right] |\psi_u(\mathbf{r}')|^2\, d\mathbf{r}d\mathbf{r}' - [\psi_g\psi_g|\psi_u\psi_u] + \mathrm{SIT}^{\mathrm{a}}$
TDHF and ΔSCF HF	$\epsilon_u^{\mathrm{HF}} - \epsilon_g^{\mathrm{HF}} + 2[\psi_g\psi_u|\psi_g\psi_u] - [\psi_g\psi_g|\psi_u\psi_u]$

	Oscillator strengths
	$f_S = \frac{4}{3} D \left(|\langle\psi_g|\hat{x}|\psi_u\rangle|^2 + |\langle\psi_g|\hat{y}|\psi_u\rangle|^2 + |\langle\psi_g|\hat{z}|\psi_u\rangle|^2 \right)$
	D
TD-DFRT	$\epsilon_u^{\mathrm{KS}} - \epsilon_g^{\mathrm{KS}}$
ΔSCF-based DFT	$\epsilon_u^{\mathrm{KS}} - \epsilon_g^{\mathrm{KS}} - \iint |\psi_g(\mathbf{r})|^2 \left[2\frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\uparrow(\mathbf{r}')} - \frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\downarrow(\mathbf{r}')} \right] |\psi_u(\mathbf{r}')|^2\, d\mathbf{r}d\mathbf{r}' - [\psi_g\psi_g|\psi_u\psi_u] + \mathrm{SIT}^{\mathrm{a}}$
TDHF	$\epsilon_u^{\mathrm{HF}} - \epsilon_g^{\mathrm{HF}} + [\psi_g\psi_u|\psi_g\psi_u] - [\psi_g\psi_g|\psi_u\psi_u]$
ΔSCF HF	$\epsilon_u^{\mathrm{HF}} - \epsilon_g^{\mathrm{HF}} + 2[\psi_g\psi_u|\psi_g\psi_u] - [\psi_g\psi_g|\psi_u\psi_u]$

[a] SIT = self-interaction terms (see text)

$$f_S^{\mathrm{DFT\ \Delta SCF}} \simeq \frac{4}{3} \left\{ \epsilon_u - \epsilon_g - \iint |\psi_g(\mathbf{r})|^2 \left[2\frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\uparrow(\mathbf{r}')} - \frac{\delta v_{\mathrm{xc}}^{\uparrow}(\mathbf{r})}{\delta\rho_\downarrow(\mathbf{r}')} \right] |\psi_u(\mathbf{r}')|^2\, d\mathbf{r}d\mathbf{r}' \right.$$
$$\left. - [\psi_g\psi_g|\psi_u\psi_u] \right\} \left(|\langle\psi_g|\hat{x}|\psi_u\rangle|^2 + |\langle\psi_g|\hat{y}|\psi_u\rangle|^2 + |\langle\psi_g|\hat{z}|\psi_u\rangle|^2 \right) . \quad (6.29)$$

However, in practical applications, the choice of orbitals to use in constructing the approximate excited state wavefunction is less clear, especially in cases where several excited state configurations, each with a different set of relaxed orbitals, are important.

The excitation energy and oscillator strength expressions from all four methods discussed are summarized in Table I. As would be expected, there is a correspondence between the DFT and HF expressions, which is obtained by replacing the Kohn–Sham exchange-correlation potential, v_{xc}, with the HF exchange operator $\hat{\Sigma}^{\mathrm{x}}$. This is manifested here in terms of a correspondence between matrix elements of the derivatives of v_{xc} and $\hat{\Sigma}^{\mathrm{x}}$,

$$\frac{\partial v_{\mu\nu\sigma}^{\mathrm{xc}}}{\partial P_{\mu'\nu'\tau}} \leftrightarrow \frac{\partial \hat{\Sigma}_{\mu\nu\sigma}^{\mathrm{x}}}{\partial P_{\mu'\nu'\tau}} , \quad (6.30)$$

which leads to both the previously noted correspondence (6.16), and

$$\iint \psi_g(\mathbf{r})\psi_g(\mathbf{r})\frac{\delta v_{\mathrm{xc}}^{\sigma}(\mathbf{r})}{\delta\rho_{\tau}(\mathbf{r'})}\psi_u(\mathbf{r'})\psi_u(\mathbf{r'})\,d\mathbf{r}d\mathbf{r'} \leftrightarrow -\delta_{\sigma,\tau}[\psi_g\psi_u|\psi_g\psi_u]\,. \tag{6.31}$$

The additional $K_{\uparrow,\uparrow}$ term in the TDHF, as compared to the TD-DFRT, oscillator strength arises from differences in $\mathcal{S}$ that come from the lower symmetry of the TDHF coupling matrix. It is interesting to note that, unlike the HF case, although the TD-DFRT and ΔSCF-based DFT excitation energy expressions are similar in structure, especially for exchange-only DFT where

$$\frac{\delta v_{\mathrm{xc}}^{\sigma}(\mathbf{r})}{\delta\rho_{\tau}(\mathbf{r'})} = \delta_{\sigma,\tau}\frac{\delta v_{\mathrm{xc}}^{\sigma}(\mathbf{r})}{\delta\rho_{\sigma}(\mathbf{r'})}\,, \tag{6.32}$$

they differ from one another in how the coulomb repulsion and exchange-correlation contributions enter into the excitation energies. In particular, the ΔSCF-based DFT excitation energy contains the coulomb integral in the same way as does HF but replaces the exchange integral in the HF expressions with a term involving the derivative of the exchange-correlation potential, whereas the TD-DFRT excitation energy contains the exchange integral in the same way as does HF but replaces the coulomb integral (which arises as the derivative of an exchange term in the derivation of the TDHF equations) with a term involving the derivative of the exchange-correlation potential.

Of course the observations in this section pertain to a highly simplified example, so some differences from a more typical case should be expected. For example, the choice of orbitals to use in ΔSCF-based DFT calculations of oscillator strengths is often somewhat ambiguous in typical applications. Nevertheless, it is clear from the foregoing discussion that TD-DFRT and the ΔSCF-based approach represent somewhat different approximations to excitation energies. This raises some interesting questions, such as whether self-interaction errors in the functionals might be more of a problem in the ΔSCF-based approach [see Eqs. (6.25) and (6.26)] than in TD-DFRT. Finally, it is evident that the ΔSCF-based DFT approach to excited states is rather *ad hoc*. In contrast, TD-DFRT lies on a firmer formal foundation, obeys the TRK sum-rule for oscillator strengths, and has the advantage of being a one-shot automatic procedure as opposed to requiring the convergence of several SCF calculations, some symmetry analysis to concoct energies for multideterminantal excited states, and occasionally the calculation of additional electron repulsion integrals not normally present in DFT calculations.

VII. Conclusion

The development of a general, time-dependent formulation of DFT has provided the formal foundation upon which a density-functional treatment of a number of properties either inaccessible or difficult to obtain using conventional time-independent DFT, can be based. Although some formal problems remain to be solved, primarily regarding restrictions on its rigorous domain of validity, the time-dependent theory already provides a reasonably solid formal framework for practical computational treatments of a number of time-dependent problems. In practice, the approach usually taken to the solution of the time-dependent DFT equations is that of (linear) response theory. Several different algorithms have been developed for atoms and for solids, each of which takes advantage of the nature of the systems it was intended to treat. The atomic algorithms use spherical symmetry in an essential way, while the solids algorithms take advantage of fast Fourier transform techniques which are well suited to a plane-wave basis. Thus none of these algorithms is suitable for molecular systems.

The present chapter has given an exposition of a time-dependent density functional response theory algorithm for molecular calculations. This method is in some ways similar to the time-dependent Hartree–Fock method which is well known in quantum chemistry, and thus can take advantage of techniques developed for other *ab initio* molecular calculations. Yet the derivation given here necessarily takes a different approach from that generally used in deriving TDHF. Also, while the Hartree–Fock method is fundamentally approximate, DFT becomes exact in the limit of the exact exchange-correlation functional. In addition, computational advantages result from the fact that only local potentials are used in DFT, and from the present use of an auxiliary function method to reduce the four-center integrals that arise in the response theory to three-center integrals. The formulation presented here is in a spin-unrestricted form and allows for fractional occupation numbers. It is also general enough to include the case of functionals beyond the adiabatic approximation, thus providing for a practical forum for the testing and further development of such functionals in the future. Although only dynamic polarizabilities and excitation spectra have been treated here, the method is readily applicable to the calculation of other properties, such as hyperpolarizabilities and van der Waals coefficients. An indication has also been given of how the theory can be extended via current density functional theory to treat time-dependent magnetic response properties.

One practical advantage of the present method for the calculation of excitation spectra is that the spectrum (transition energies and oscillator strengths) is obtained all at once, as the solution of a pseudo-eigenvalue problem, as opposed to the ΔSCF-based DFT approach to excited states which involves doing separate calculations for each excited state. There are other noteworthy differences between the *ad hoc* ΔSCF-based approach to spectra and the present TD-DFRT method as well. For instance, as was illustrated for the simple, minimal basis, H_2 example, the ΔSCF-based approach (using the transition state method) and TD-DFRT represent somewhat different approximations for the excitation energy and oscillator strength. In addition, the "multiplet problem" of the ΔSCF-based approach is not encountered in TD-DFRT which includes a multiconfigurational treatment of the excited states in a natural way.

The method set forth here is presently being implemented as a post-deMon program DynaRho (for "Dynamical Response of ρ"). The results so far, for the excitation spectra of half a dozen small molecules, at different levels of approximation, are highly encouraging. Preliminary results for the dynamic polarizability and excitation spectrum of N_2, a benchmark molecule for the calculation of electronic spectra, have been reported elsewhere [51], at the level of the random phase approximation (RPA), which consists of including only the coulomb term, and neglecting the exchange-correlation term, in the coupling matrix. (It is only the *response* of the exchange-correlation potential that is neglected in the RPA, exchange and correlation are still included in the calculation of the zero-order orbitals and orbital energies.) At this level of approximation, the singlet-triplet excitations have no coupling, but the singlet-singlet excitation energies of N_2 are already better than those obtained from TDHF. Results at the fully coupled level will be reported in a forthcoming paper [71].

In view of the computational advantages of the TD-DFRT approach, and the quality of the results to date, this method promises to become a powerful, practical technique for the investigation of the optical properties of larger molecules than is possible with other *ab initio* methods.

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