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Adiabatic time-dependent density functional methods for excited state properties

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This work presents theory, implementation, and validation of excited state properties obtained from time-dependent density functional theory (TDDFT). Based on a fully variational expression for the excited state energy, a compact derivation of first order properties is given. We report an implementation of analytic excited state gradients and charge moments for local, gradient corrected, and hybrid functionals, as well as for the configuration interaction singles (CIS) and time-dependent Hartree–Fock (TDHF) methods. By exploiting analogies to ground state energy and gradient calculations, efficient techniques can be transferred to excited state methods. Benchmark results demonstrate that, for low-lying excited states, geometry optimizations are not substantially more expensive than for the ground state, independent of the molecular size. We assess the quality of calculated adiabatic excitation energies, structures, dipole moments, and vibrational frequencies by comparison with accurate experimental data for a variety of excited states and molecules. Similar trends are observed for adiabatic excitation energies as for vertical ones. TDDFT is more robust than CIS and TDHF, in particular, for geometries differing significantly from the ground state minimum. The TDDFT excited state structures, dipole moments, and vibrational frequencies are of a remarkably high quality, which is comparable to that obtained in ground state density functional calculations. Thus, yielding considerably more accurate results at similar computational cost, TDDFT rivals CIS as a standard method for calculating excited state properties in larger molecules. © 2002 American Institute of Physics. [DOI: 10.1063/1.1508368]

I. INTRODUCTION

There is a broad interest in properties of electronic excited states ranging from spectroscopy to photochemistry and biology.^{1,2} In fact, for a deeper understanding of most photophysical and photochemical phenomena, some information on excited state potential energy surfaces is necessary. For example, luminescence and related emission processes are associated with geometric relaxation of excited states. It is also well known that structural changes upon electronic excitation can significantly alter the shape of absorption and circular dichroism spectra. According to the Franck–Condon principle, knowledge of the excited state normal modes is required to describe the fine structure observed in high-resolution spectra. Vibrations may induce forbidden transitions, or mediate nonadiabatic coupling. Information on structure and dynamics of excited states is the most important prerequisite for modeling photochemical reactions.³

With the development of new techniques in laser spectroscopy,⁴ excited state properties, e.g., vibrational frequencies or dipole moments, can be probed selectively for increasingly large systems. Reliable theoretical models are necessary, however, to explain the experimental data in terms of the excited state geometric and electronic structure. Up to now, the standard for calculating excited state equilibrium properties of larger molecules is the configuration interaction singles (CIS) method.^{5,6} However, due to a neglect of electron correlation, CIS results are not accurate enough in many

applications.⁷ In the past five years, time-dependent density functional theory (TDDFT)⁸ has almost completely superseded CIS in *vertical* excitation energy calculations, yielding considerably improved results at similar computational cost.^{9–11} The pioneering work of Amos and Van Caillie^{12,13} and recent case studies^{14,15} indicate that TDDFT may be more accurate than CIS for excited state potential energy surfaces and other properties as well.

A number of state-based density functional methods has been proposed for excited state treatments;^{16–18} for the lowest excited singlet state, a spin-restricted open-shell Kohn–Sham (KS) type scheme has been proposed.¹⁹ It largely remains to be shown that these methods are competitive to TDDFT in standard applications. Judging from experience with wave-function methods,²⁰ advantages of TDDFT, such as a consistent definition of transition moments and the explicit treatment of near-degeneracy effects between singly excited configurations, will not be easily overcome.

The purpose of the present work is threefold. First, we give a TDDFT excited state energy functional which is fully variational with respect to all parameters. This considerably simplifies the derivation of analytic expressions for first order excited state properties. We extend the theory for general spin-unrestricted ground states, recovering previous results for CIS,⁵ time-dependent Hartree–Fock (TDHF),²¹ and TDDFT¹³ as special cases. Second, we describe an efficient implementation of excited state gradients with respect to nuclear coordinates and other first order properties for the above methods. In contrast to numerical differentiation, the

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effort for calculating gradients analytically is independent of the number of nuclear degrees of freedom. We emphasize the analogy to ground state energy and gradient calculations, which allows us to transfer proven techniques to excited state methods. The feasibility of excited state geometry optimizations is investigated in typical applications. Finally, we assess the quality of calculated adiabatic excitation energies, excited state dipole moments, structures, and vibrational frequencies by comparison with accurate experimental data. Our test sample contains a variety of states of different character and spin multiplicity. The methods include, besides CIS and TDHF, the most popular functionals used in TDDFT calculations. We analyze the results and discuss implications for theoretical treatments of excited states.

II. THEORY

A. Excited state properties in TDDFT

The variational formulation of TDDFT (Ref. 22) provides a very convenient framework for the calculation of excited state properties. The basic statement is that excitation energies are the stationary points of the functional

$$G[X, Y, \Omega] = \langle X, Y | \Lambda | X, Y \rangle - \Omega (\langle X, Y | \Delta | X, Y \rangle - 1). \quad (1)$$

Ω is a real Lagrange multiplier, and the vectors

$$|X, Y\rangle = \begin{pmatrix} X \\ Y \end{pmatrix} \quad (2)$$

are defined on the Hilbert space $L = L_{\text{virt}} \times L_{\text{occ}} \oplus L_{\text{occ}} \times L_{\text{virt}}$, where L_{occ} and L_{virt} denote the Hilbert spaces of occupied (occ) and virtual (virt) molecular orbitals (MOs), respectively. The MOs $\varphi_{p\sigma}(\mathbf{r})$ are solutions of the static KS equations with eigenvalues $\epsilon_{p\sigma}$. As usual, indices i, j, \dots label occupied, a, b, \dots virtual, and p, q, \dots general MOs. We assume the MOs to be real, which is always possible in the absence of magnetic fields. The ‘‘superoperators’’ Λ and Δ read

$$\Lambda = \begin{pmatrix} A & B \\ B & A \end{pmatrix}, \quad \Delta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (3)$$

A and B are sometimes called orbital rotation Hessians and have the matrix representation

$$\begin{aligned} (A+B)_{ia\sigma jb\sigma'} &= (\epsilon_{a\sigma} - \epsilon_{i\sigma}) \delta_{ij} \delta_{ab} \delta_{\sigma\sigma'} \\ &\quad + 2(ia\sigma | jb\sigma') + 2f_{ia\sigma jb\sigma'}^{\text{xc}} \\ &\quad - c_x \delta_{\sigma\sigma'} [(ja\sigma | ib\sigma) + (ab\sigma | ij\sigma)], \end{aligned} \quad (4a)$$

$$\begin{aligned} (A-B)_{ia\sigma jb\sigma'} &= (\epsilon_{a\sigma} - \epsilon_{i\sigma}) \delta_{ij} \delta_{ab} \delta_{\sigma\sigma'} + c_x \delta_{\sigma\sigma'} [(ja\sigma | ib\sigma) \\ &\quad - (ab\sigma | ij\sigma)]. \end{aligned} \quad (4b)$$

$(pq\sigma | rs\sigma')$ is a two-electron repulsion integral in Mulliken notation, and $f_{pq\sigma rs\sigma'}^{\text{xc}}$ represents a matrix element of the exchange-correlation kernel in the adiabatic approximation,

$$f_{\sigma\sigma'}^{\text{xc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E^{\text{xc}}}{\delta \rho_{\sigma}(\mathbf{r}) \delta \rho_{\sigma'}(\mathbf{r}')}. \quad (5)$$

E^{xc} denotes the static exchange-correlation energy functional; the functional derivative is evaluated, as all other

functionals in the present work, at the static ground state density. The hybrid mixing parameter c_x introduced by Becke^{23,24} allows us to interpolate between the limits of ‘‘pure’’ density functionals ($c_x=0$) and TDHF theory ($c_x=1$, $E^{\text{xc}}=0$), which is also known as the random phase approximation (RPA) for excitation energies.²⁵ The CIS or Tamm–Dancoff approximation (TDA) is easily derived by constraining Y identically to zero in the variation of G . A TDA type scheme has recently been proposed in a TDDFT context as well.¹¹ All these methods are contained as special cases in the present approach.

Applying the variational principle, we obtain the stationarity conditions for G ,

$$\frac{\delta G}{\delta \langle X, Y |} = (\Lambda - \Omega \Delta) | X, Y \rangle = 0, \quad (6a)$$

$$\frac{\partial G}{\partial \Omega} = \langle X, Y | \Delta | X, Y \rangle - 1 = 0. \quad (6b)$$

Equation (6a) is the well-known time-dependent Kohn–Sham (TDKS) eigenvalue problem; solution under constraint (6b) yields the TDDFT excitation energies as eigenvalues Ω and TDKS transition density matrices as eigenvectors $|X, Y\rangle$. Unless stated otherwise, we shall assume in the following that Eqs. (6a) and (6b) have been solved for a particular excited state under consideration.

In analogy to ground state properties, excited state properties are conveniently defined as derivatives of the excited state energy with respect to an external perturbation.²⁶ These derivatives are, somewhat symbolically, denoted by a superscript ξ . We think of ξ as a nuclear coordinate in the first place, leading to excited state energy gradients with respect to the positions of the nuclei. However, other excited state properties are accessible as well. If ξ represents, e.g., a component of a static electric field, excited state dipole moments can be computed. The total excited state energy is the sum of the ground state energy and the excitation energy. Thus, excited state properties are a sum of the corresponding ground state properties and an excitation part given by derivatives of the excitation energy. We can focus on the latter here since the computation of HF and KS ground state properties is certainly well established. In terms of the functional G defined in Eq. (1),

$$\Omega^\xi = G^\xi[X, Y, \Omega] = \langle X, Y | \Lambda^\xi | X, Y \rangle. \quad (7)$$

It is important to note that due to the variational principle, first order properties do *not* require derivatives of the excitation vectors $|X, Y\rangle$. If f denotes the number of nuclear degrees of freedom in a molecule, computing first derivatives of $|X, Y\rangle$ would be roughly f times as expensive as a single-point excitation energy calculation.

However, a straightforward calculation of Λ^ξ still involves derivatives of the MO coefficients. In basis set methods, the MOs are usually expanded as a linear combination of atomic orbitals (LCAO),

$$\varphi_{p\sigma}(\mathbf{r}) = \sum_{\mu} C_{\mu p\sigma} \chi_{\mu}(\mathbf{r}). \quad (8)$$

A MO $\varphi_{p\sigma}$ can depend on the perturbation through the atomic orbitals (AOs) $\chi_{\mu}(\mathbf{r})$ and the expansion coefficients C . Derivatives of the basis functions $\chi_{\mu}(\mathbf{r})$ are easily dealt with: In case ξ denotes a nuclear coordinate, the derivatives $\chi_{\mu}^{\xi}(\mathbf{r})$ are nonzero only if ξ refers to the atom $\chi_{\mu}(\mathbf{r})$ is centered at. The MO coefficients, though, depend on all f perturbations in general, so that a calculation of the derivatives C^{ξ} would require f times the work of a calculation of the unperturbed MOs. Fortunately, it is possible to eliminate derivatives C^{ξ} by introducing so-called relaxed densities, at a computational cost independent of f . This is a consequence of the Sternheimer–Dalgarno interchange theorem,^{27,28} which is better known as the Z vector method²⁹ in quantum chemistry. However, the introduction of perturbed MO coefficients leads to lengthy expressions that have to be rearranged in a nontrivial way in order to apply the Z vector method. Although tedious, this procedure has previously been used to derive excited state gradients for CIS,⁵ TDHF,²¹ and TDDFT^{12,13} methods.

B. Lagrangian of the excitation energy

We pursue a different strategy which avoids MO coefficient derivatives from the very beginning instead of first introducing them and reeliminating them later. In a first step, we replace the diagonal part of $(A+B)$ and $(A-B)$ in Eqs. (4a) and (4b) by

$$(F_{ab\sigma} \delta_{ij} - F_{ij\sigma} \delta_{ab}) \delta_{\sigma\sigma'}. \quad (9)$$

The effective KS one-particle Hamiltonian or Fock operator

$$F_{pq\sigma} = h_{pq\sigma} + \sum_{i\sigma'} [(pq\sigma|ii\sigma') - c_x \delta_{\sigma\sigma'} (pi\sigma|iq\sigma)] + V_{pq\sigma}^{\text{xc}}, \quad (10)$$

consists of the core Hamilton h , a Coulomb and (hybrid-) exchange part, and the exchange-correlation potential

$$V_{\sigma}^{\text{xc}}(\mathbf{r}) = \frac{\delta E^{\text{xc}}}{\delta \rho_{\sigma}(\mathbf{r})}. \quad (11)$$

In the basis of canonical KS MOs, F is diagonal with the eigenvalues $\epsilon_{p\sigma}$ as diagonal entries. This choice is somewhat arbitrary, though, since all physical properties are invariant under unitary transformations of occupied and virtual orbitals among themselves. The above replacement renders the excited state formalism manifestly invariant under these transformations. The constraint of a canonical choice of the MOs can thus be dropped when calculating derivatives of the excitation energy.

In a slight variation of an idea of Helgaker and Jørgensen,³⁰ we define the auxiliary functional

$$L[X, Y, \Omega, C, Z, W] = G[X, Y, \Omega] + \sum_{i\sigma} Z_{i\sigma} F_{i\sigma} - \sum_{pq\sigma, p \leq q} W_{pq\sigma} (S_{pq\sigma} - \delta_{pq}). \quad (12)$$

The Lagrangian L is required to be stationary with respect to all its parameters, X , Y , Ω , C , Z , and W , which are considered as variables in Eq. (12). The sum of the ground state Lagrangian and L thus represents a fully variational expression for the excited state energy functional. Similar techniques have been used in correlated treatments of excited state properties.³¹ While variation of L with respect to $|X, Y\rangle$ and Ω leads back to Eqs. (6), the additional Lagrange multipliers Z and W enforce the conditions

$$\frac{\partial L}{\partial Z_{i\sigma}} = F_{i\sigma} = 0, \quad (13)$$

$$\frac{\partial L}{\partial W_{pq\sigma}} = S_{pq\sigma} - \delta_{pq} = 0. \quad (14)$$

The MOs $\varphi_{p\sigma}(\mathbf{r})$ are thus constrained to satisfy the static KS equations (up to unitary equivalence), and to be orthonormal. These conditions fix the MO coefficients C for all values of the external perturbation. Z and W themselves are determined from the condition

$$\frac{\partial L}{\partial C_{\mu p\sigma}} = 0, \quad (15)$$

as shown in detail below. Solving Eq. (15) is approximately f times more efficient than computing perturbed MO coefficients.

At first sight, the definition of excitation energies as stationary points of L appears to be more complicated than the definition as stationary points of G , because additional parameters have been introduced. However, while G depends implicitly through the MO coefficients on an external perturbation, this implicit dependence drops out of L by virtue of the variational principle. Thus, L is an explicit functional of any external perturbation. This is a crucial advantage in the treatment of excited state properties: Once X , Y , Ω , C , Z , and W have been determined from the stationarity conditions, derivatives of the excitation energy follow as

$$\begin{aligned} \Omega^{\xi} &= L^{\xi}[X, Y, \Omega, C, Z, W] \\ &= G^{(\xi)}[X, Y, \Omega] + \sum_{i\sigma} Z_{i\sigma} F_{i\sigma}^{(\xi)} - \sum_{pq\sigma, p \leq q} W_{pq\sigma} S_{pq\sigma}^{(\xi)}. \end{aligned} \quad (16)$$

In contrast to Eq. (7), the derivatives are straightforward to evaluate, because the MO coefficients C are held constant at their zero order values, as indicated by the superscript (ξ) . This is especially obvious for the contribution

$$\begin{aligned} G^{(\xi)}[X, Y, \Omega] &= \langle X, Y | \Lambda^{(\xi)} | X, Y \rangle \\ &= \frac{1}{2} \sum_{i\sigma, j\sigma'} [(A+B)_{i\sigma, j\sigma'}^{(\xi)} (X+Y)_{i\sigma} (X+Y)_{j\sigma'} \\ &\quad + (A-B)_{i\sigma, j\sigma'}^{(\xi)} (X-Y)_{i\sigma} (X-Y)_{j\sigma'}]. \end{aligned} \quad (17)$$

C. Determination of the Lagrange multipliers Z and W

The orbital stationarity constraint (15) gives rise to four conditions for Z and the various parts of W . A detailed derivation is given in Appendix A; we merely state the results here. For Z one obtains

$$\sum_{jb\sigma'} (A+B)_{ia\sigma j b\sigma'} Z_{j b\sigma'} = -R_{ia\sigma}, \quad (18)$$

which is traditionally called the Z vector equation. Defining the unrelaxed difference density matrix T

$$T_{ab\sigma} = \frac{1}{2} \sum_i \{ (X+Y)_{ia\sigma} (X+Y)_{ib\sigma} + (X-Y)_{ia\sigma} (X-Y)_{ib\sigma} \}, \quad (19)$$

$$T_{ij\sigma} = -\frac{1}{2} \sum_a \{ (X+Y)_{ia\sigma} (X+Y)_{ja\sigma} + (X-Y)_{ia\sigma} (X-Y)_{ja\sigma} \},$$

$$T_{ia\sigma} = T_{ai\sigma} = 0,$$

and, for arbitrary vectors $V_{pq\sigma}$, the linear transformations

$$H_{pq\sigma}^+[V] = \sum_{rs\sigma'} \{ 2(pq\sigma|rs\sigma') + 2f_{pq\sigma rs\sigma'}^{\text{xc}} - c_x \delta_{\sigma\sigma'} \} \times [(ps\sigma|rq\sigma) + (pr\sigma|sq\sigma)] V_{rs\sigma}, \quad (20a)$$

$$H_{pq\sigma}^-[V] = \sum_{rs\sigma'} c_x \delta_{\sigma\sigma'} [(ps\sigma|rq\sigma) - (pr\sigma|sq\sigma)] V_{rs\sigma}, \quad (20b)$$

the right-hand side (RHS) R is conveniently expressed as

$$\begin{aligned} R_{ia\sigma} = & \sum_b \{ (X+Y)_{ib\sigma} H_{ab\sigma}^+[X+Y] \\ & + (X-Y)_{ib\sigma} H_{ab\sigma}^-[X-Y] \} \\ & - \sum_j \{ (X+Y)_{ja\sigma} H_{ji\sigma}^+[X+Y] \\ & + (X-Y)_{ja\sigma} H_{ji\sigma}^-[X-Y] \} + H_{ia\sigma}^+[T] \\ & + 2 \sum_{jb\sigma' kc\sigma''} g_{ia\sigma j b\sigma' kc\sigma''}^{\text{xc}} (X+Y)_{j b\sigma'} (X+Y)_{k c\sigma''}. \end{aligned} \quad (21)$$

$g_{pq\sigma rs\sigma' tu\sigma''}^{\text{xc}}$ denotes a matrix element of the third order functional derivative

$$g_{\sigma\sigma'\sigma''}^{\text{xc}}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \frac{\delta^3 E^{\text{xc}}}{\delta\rho_{\sigma}(\mathbf{r}) \delta\rho_{\sigma'}(\mathbf{r}') \delta\rho_{\sigma''}(\mathbf{r}'')}. \quad (22)$$

From Eq. (21) it appears that the computation of R is rather involved; however, as discussed in Sec. III, it is never necessary to set up and store more than two-index quantities.

After the Z vector Eq. (18) has been solved, the relaxed one-particle difference density matrix P is obtained as

$$P = T + Z, \quad (23)$$

where the occ-occ and virt-virt parts of Z are zero. The physical meaning of P will become obvious in the next subsection. The remaining conditions from Eq. (15) fix the Lagrange multipliers W according to

$$\begin{aligned} W_{ij\sigma} = & \sum_a \Omega \{ (X+Y)_{ia\sigma} (X-Y)_{ja\sigma} + (X-Y)_{ia\sigma} \\ & \times (X+Y)_{ja\sigma} \} - \sum_a \epsilon_{a\sigma} \{ (X+Y)_{ia\sigma} (X+Y)_{ja\sigma} \\ & + (X-Y)_{ia\sigma} (X-Y)_{ja\sigma} \} + H_{ij\sigma}^+[P] \\ & + 2 \sum_{kc\sigma' ld\sigma''} g_{ij\sigma kc\sigma' ld\sigma''}^{\text{xc}} (X+Y)_{k c\sigma'} (X+Y)_{l d\sigma''}, \\ W_{ab\sigma} = & \sum_i \Omega \{ (X+Y)_{ia\sigma} (X-Y)_{ib\sigma} \\ & + (X-Y)_{ia\sigma} (X+Y)_{ib\sigma} \} \\ & + \sum_i \epsilon_{i\sigma} \{ (X+Y)_{ia\sigma} (X+Y)_{ib\sigma} \\ & + (X-Y)_{ia\sigma} (X-Y)_{ib\sigma} \}, \end{aligned} \quad (24)$$

$$\begin{aligned} W_{ia\sigma} = & \sum_j \{ (X+Y)_{ja\sigma} H_{ji\sigma}^+[X+Y] \\ & + (X-Y)_{ja\sigma} H_{ji\sigma}^-[X-Y] \} + \epsilon_{i\sigma} Z_{ia\sigma}. \end{aligned}$$

W will turn out as the energy-weighted difference density matrix below.

D. First order properties of excited states

Using the definitions of A , B , and F , Eq. (16) is easily transformed into the final form

$$\begin{aligned} \Omega^\xi = & \sum_{\mu\nu\sigma} h_{\mu\nu}^\xi P_{\mu\nu\sigma} - \sum_{\mu\nu\sigma} S_{\mu\nu}^\xi W_{\mu\nu\sigma} + \sum_{\mu\nu\sigma} V_{\mu\nu\sigma}^{\text{xc}(\xi)} P_{\mu\nu\sigma} \\ & + \sum_{\mu\nu\kappa\lambda\sigma\sigma'} (\mu\nu|\kappa\lambda)^\xi \Gamma_{\mu\nu\sigma\kappa\lambda\sigma'} \\ & + \sum_{\mu\nu\kappa\lambda\sigma\sigma'} f_{\mu\nu\sigma\kappa\lambda\sigma'}^{\text{xc}(\xi)} (X+Y)_{\mu\nu\sigma} (X+Y)_{\kappa\lambda\sigma'}. \end{aligned} \quad (25)$$

Greek indices indicate that operator matrix elements are taken in the AO basis, and

$$V_{\mu\nu\sigma} = \sum_{pq} C_{\mu p\sigma} V_{pq\sigma} C_{\nu q\sigma}, \quad (26)$$

for $V=P$, W , and $(X\pm Y)$. If D denotes the ground state density matrix, the effective two-particle difference density matrix is given by

$$\begin{aligned} \Gamma_{\mu\nu\sigma\kappa\lambda\sigma'} = & \frac{1}{2}\{2P_{\mu\nu\sigma}D_{\kappa\lambda\sigma'} + 2(X+Y)_{\mu\nu\sigma}(X+Y)_{\kappa\lambda\sigma'} \\ & - c_x\delta_{\sigma\sigma'}[P_{\mu\lambda\sigma}D_{\kappa\nu\sigma'} + P_{\mu\kappa\sigma}D_{\lambda\nu\sigma'} \\ & + (X+Y)_{\mu\lambda\sigma}(X+Y)_{\kappa\nu\sigma'} \\ & + (X+Y)_{\mu\kappa\sigma}(X+Y)_{\lambda\nu\sigma'} \\ & - (X-Y)_{\mu\lambda\sigma}(X-Y)_{\kappa\nu\sigma'} \\ & + (X-Y)_{\mu\kappa\sigma}(X-Y)_{\lambda\nu\sigma'}\}]; \end{aligned} \quad (27)$$

the various direct and exchange contributions thus separate into products of lower rank quantities, which is important for the processing of Γ .

Equation (25) indicates that, after spin summation, P , W , and Γ may be regarded as partial derivatives of the excitation energy with respect to $h_{\mu\nu}$, $S_{\mu\nu}$, and the electron–electron interaction. All first order properties can be expressed in the form of Eq. (25) since the excitation energy can depend on an external perturbation only through h , S , the electron–electron interaction, and the exchange–correlation functional derivatives. For example, the difference between the excited and ground state dipole moments follows as

$$\Delta\langle\boldsymbol{\mu}\rangle = \text{tr}(P\boldsymbol{\mu}), \quad (28)$$

if $\boldsymbol{\mu}$ denotes the dipole moment operator. Population analysis of P can elucidate the charge rearrangement and the change in bond order induced by an electronic excitation. This is complementary to the information supplied by the vectors $|X, Y\rangle$, which describe the excitation in terms of occupied and virtual MOs, i.e., the change in the electronic structure. The Z vector contribution to P in Eq. (23), which accounts for orbital relaxation effects, is often of the same order of magnitude as the “unrelaxed” part T and cannot be neglected, in contrast to what has occasionally been assumed.³²

We note in passing that, in analogy to the ground state KS scheme, P would yield the exact density difference if the exact (time-dependent) exchange–correlation functional were used. This follows from the fact that the density computed from P is identical to the functional derivative of the excitation energy with respect to a local external potential.

III. IMPLEMENTATION

A. General strategy

The results of the last section suggest that the analytic computation of excited state energy gradients and other properties should be organized as follows: Given the solution of the ground state KS equations,

- (1) determine the excitation energy Ω and excitation vector $|X, Y\rangle$ from Eqs. (6);
- (2) solve the Z vector Eq. (18) to obtain the Lagrange multipliers Z and W ; and
- (3) evaluate the gradient and other properties according to Eq. (25).

Methods for solving the TDKS eigenvalue problem (6a) and the static coupled KS Eqs. (18) are well developed.^{10,33–35} In an iterative integral direct algorithm, the operations neces-

sary in each iteration closely resemble those for a single ground state Fock matrix construction. If N is a measure of the system size, the use of integral prescreening leads to an asymptotic scaling of computational cost proportional to N^2 for the Coulomb and hybrid exchange contributions, while (nearly) linear scaling of the exchange–correlation contribution is achieved by efficient molecular quadrature schemes.^{36,37} The total effort for steps (1) and (2) is thus comparable to solving the ground state KS equations. For higher excited states the first step becomes increasingly expensive, since all lower states of the same symmetry have to be calculated as well. This is not a significant limitation, however, since in the majority of applications highly excited states do not play an important role.

Step (3), evaluation of the gradient, is largely identical to the analytic computation of ground state gradients. In fact, apart from the exchange–correlation terms discussed below, only the expressions for the one- and two-particle density matrix as well as the energy-weighted density matrix have to be replaced by P , W , and Γ . By adding the ground state contributions to P , W , and Γ before evaluating Eq. (25), gradients of the total excited state energy can be obtained in a one-step procedure. The cost for step (3) is thus virtually identical to that for ground state gradients.

To sum up, following the method outlined above, the effort for an excited state geometry optimization is not substantially higher than for a ground state geometry optimization. It is important to stress the similarity to the computation of the ground state energy and gradient since this implies that the whole arsenal of efficient techniques for ground states is applicable to excited states, too. If there is progress in ground state methods, excited state methods will also benefit. Finally, given a code for TDDFT excitation energies and response properties as well as a ground state gradient code, excited state gradients can be implemented by minor modifications.

B. Exchange–correlation contributions

The only terms which are not straightforward to transfer from ground state and linear response calculations are those containing third-order functional derivatives [Eqs. (21) and (24)] and geometric derivatives of the exchange–correlation potential and kernel [Eq. (25)]. However, scrutiny of these contributions reveals that they can be reduced to the same form as $V_{\mu\nu\sigma}^{\text{xc}}$ and $E^{\text{xc}(\xi)}$, both routinely computed in ground state energy and gradient calculations. To put this into more explicit terms, consider the exchange–correlation energy functional within the generalized gradient approximation (GGA),

$$E^{\text{xc}} = \int d^3r f(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}), \quad (29)$$

where $\gamma_{\sigma\sigma'} = \nabla\rho_\sigma \nabla\rho_{\sigma'}$. The local density approximation (LDA), where f depends only on the spin densities ρ_α and ρ_β , is a special case of the GGA. Now, the matrix of the exchange–correlation potential is computed by numerical quadrature of

TABLE I. Survey of the exchange-correlation energy functionals used in this work.

Name	Type	Exchange	Correlation	Ref.
SVWN	LDA	S	VWN	52–54
PW	LDA	S	PW	55
BLYP	GGA	S+B88	LYP	56, 57
BP86 ^a	GGA	S+B88	VWN+P86	58
PBE	GGA	S+PBE(X)	PW+PBE(C)	59
PBE0	hybrid	0.25 HF+0.75 [S+PBE(X)]	PW+PBE(C)	60
B3LYP ^b	hybrid	0.2 HF+0.72 B88+0.8 S	0.19 VWN+0.81 LYP	24

^aThe BP86 implementation in TURBOMOLE and CADPAC differs from that in GAUSSIAN and Q-CHEM by the LDA correlation part, which is VWN instead of PZ81 (Ref. 61).

^bAt variance with the GAUSSIAN and Q-CHEM programs, we use the full (beyond RPA) VWN parametrization in the spin-polarized case (also called VWN-V), as recommended by VWN.

$$V_{\mu\nu\sigma}^{\text{xc}} = \int d^3r \left(\frac{\partial f}{\partial \rho_\sigma} + 2 \frac{\partial f}{\partial \gamma_{\sigma\sigma'}} \nabla \rho_\sigma \nabla \right. \\ \left. + \frac{\partial f}{\partial \gamma_{\sigma\sigma'}} \nabla \rho_{\sigma'} \nabla \right) \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}), \quad (30)$$

and the partial derivatives of E^{xc} are calculated as

$$E^{\text{xc}}(\xi) = \int d^3r \sum_\sigma \left(\frac{\partial f}{\partial \rho_\sigma} + 2 \frac{\partial f}{\partial \gamma_{\sigma\sigma'}} \nabla \rho_\sigma \nabla \right. \\ \left. + \frac{\partial f}{\partial \gamma_{\sigma\sigma'}} \nabla \rho_{\sigma'} \nabla \right) \rho_\sigma^{(\xi)}(\mathbf{r}), \quad (31)$$

where $\sigma' \neq \sigma$, as is of course well known.^{36,38} The contributions necessary for excited state gradients are obtained by formally replacing first derivatives of f by second and third derivatives, multiplied by an effective density and its gradients on the quadrature grid. The latter is given by

$$\sum_{\mu\nu} (X+Y)_{\mu\nu\sigma} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}), \quad (32)$$

i.e., the first order density response, for the terms containing second and third functional derivatives, and by

$$\sum_{\mu\nu} P_{\mu\nu\sigma} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}), \quad (33)$$

i.e., the difference density, for the contribution from $V_{\mu\nu\sigma}^{\text{xc}}(\xi)$ in Eq. (25). The only additional operations required for excited state gradient calculations are thus the evaluation of the effective densities and the second and third derivatives of f . Analytic implementation of the latter for the GGA functionals used in this work is tedious, but elementary.

C. The program EGRAD

Following the strategy outlined in Sec. III A, TDDFT excited state gradients have been implemented in the new module EGRAD, which is part of the TURBOMOLE program suite.³⁹ A survey of the most important functionals currently available and used in this work is given in Table I; in addition, the CIS and TDHF methods are available. We fully exploit molecular point group symmetry for all finite point groups (with less than 100-fold symmetry axes), thus saving a factor of approximately the order of the point group in computation time and disk space requirements. Spin symmetry is also taken into account for spin restricted closed shell

ground states. As is well known, in this case distinguishing between singlet and triplet excitations further reduces CPU and storage requirements by a factor of 2. Nevertheless, EGRAD can also deal with general spin unrestricted open shell references, thus permitting the treatment of excited states of radicals. We have carefully checked the correctness of our implementation by comparison with results from numerical differentiation.

In Table II we give some representative CPU timings for the calculation of the excited state energy+gradient and compare them to timings for ground state energies. The numbers show that geometry optimizations for lower excited states are not significantly more expensive than ground state geometry optimizations. The asymptotic scaling of computational cost is approximately proportional to N^2 , thus allowing for rather large applications already. The time-determining step, computation and processing of the two-electron repulsion integrals, can be further accelerated by means of the resolution of the identity (RI) technique;^{40,41} work along these lines is in progress.

IV. COMPUTATIONAL DETAILS

The structures of the molecules considered below were optimized in the ground and excited states (energy change

TABLE II. CPU timings (hours) for single point ground state energies (DSCF) and single point excitation energies+excited state gradients (EGRAD). The calculations were performed on a single CPU of an HP J240 workstation (240 MHz). Start orbitals were generated by extended Hückel theory, and a convergence of the ground state density matrix to 10^{-7} a.u. was required. Quadrature grids were of size 3 (Ref. 36). N_{BF} denotes the number of contracted Gaussian basis functions. The basis sets are described in Sec. IV.

System	Sym.	State	Funct.	Basis	N_{BF}	DSCF	EGRAD
<i>trans</i> -stilbene	C_{2h}	1^1B_u	B3LYP	SVP	270	0:13	0:23
Triphenylmethyl ^a	C_3	1^2E	BP	SVP	360	0:18	0:32
[6]Helicene	C_2	1^3A	BP	SV(P)	422	1:22	1:17
DMABN ^b	C_{2v}	2^1A_1	BP	TZVPP	546	2:25	2:54
Retinal	C_1	2^1A	PBE	SVP	455	2:33	2:28
(AlCp*) ₄ ^c	D_{2d}	1^1E	BP	SV(P)	796	2:33	2:30

^aOpen shell.

^b4-(dimethylamino)benzonitrile.

^c Cp^* =pentamethylcyclopentadienyl.

TABLE III. Basis set dependence of the calculated properties of the $1^1A''$ excited state of CH_2O . The TDHF method is used. Energies E are in Hartree, excitation energies T_e in eV, bond lengths in pm, out-of-plane angles ϕ in degrees, and dipole moments μ in D.

Basis	E	T_e	C–O	C–H	ϕ	μ
SVP	-113.620 440	4.336	125.33	109.43	26.14	1.411
aug-SVP	-113.629 459	4.356	125.04	109.38	24.21	1.350
aug-TZVP	-113.754 481	4.328	125.25	108.68	25.56	1.290
TZVPP	-113.758 247	4.365	124.96	108.59	25.89	1.324
aug-TZVPP	-113.759 062	4.363	124.86	108.61	24.45	1.285
aug-cc-pVQZ	-113.762 254	4.372	124.75	108.57	24.47	1.282

$\leq 10^{-6}$ Hartree, maximum gradient norm $\leq 10^{-3}$ a.u.). The ground state energy and density matrix were converged to at least 10^{-7} a.u.; fine quadrature grids [size 4 (Ref. 36)] were used. Harmonic vibrational frequencies and zero point energies (ZPEs) were determined by numerical differentiation of the analytic gradients (central differences, default displacements 0.02 bohr). T_e values were obtained as energy differences between the excited and ground states in their equilibrium structures, T_0 values include ZPE differences. All calculated T_0 values, structural parameters, dipole moments, and frequencies were obtained in the harmonic approximation.

In order to assess the basis set dependence of the calculated excited state properties, we have optimized the $1^1A''$ state of CH_2O in various basis sets, see Table III. SV denotes split valence⁴² and TZV triple zeta valence⁴³ basis sets; P is a single set of polarization functions, and PP a double one, e.g., $2d1f$ for elements C–F. The prefix “aug” stands for sets of diffuse basis functions⁴⁴ containing an additional primitive Gaussian for each l -quantum number in the original basis set. The aug-cc-pVQZ basis set^{45,46} is of quadruple zeta valence quality, with three sets of polarization functions and diffuse augmentation. The results in Table III were obtained using TDHF, but the other methods are expected to exhibit very similar basis set dependence.

The diffuse augmentation has little influence on the energy of the rather compact $1^1A''$ state, but is necessary for an accurate description of the geometry. Considering the convergence of both energy and properties, a hierarchy of basis sets for excited state calculations is

$$\text{aug-SVP} < \text{aug-TZVPP} < \text{aug-cc-pVQZ}. \quad (34)$$

This is not unexpected from the experience with ground state calculations and other response properties such as polarizabilities. The energy convergence indicates that the aug-cc-pVQZ results are close to the basis set limit. From Table III, we estimate the basis set errors for aug-TZVPP to be approximately ± 0.02 eV in the excitation energy, ± 0.2 pm in bond lengths and ± 0.02 D in the dipole moment (for the $1^1A''$ state of CH_2O). Since this appears quite sufficient for our present purpose, all calculations were performed using the aug-TZVPP basis set, unless stated otherwise. For the elements Li, Be, Mg, Sc, and Cu, Dunning diffuse functions are not available. We, therefore, have constructed basis sets of quality comparable to aug-TZVPP by augmenting stan-

TABLE IV. Basis sets of aug-TZVPP quality for the elements Li, Be, Mg, Sc, and Cu. We list the names of the corresponding standard basis sets from the TURBOMOLE library (see Refs. 42, 43, and 62) as well as the primitive Gaussians added. Exponents obtained from downward extrapolation are designated by E.

Element	Basis	Augmentation		Remarks
		l	Exponent	
Li	TZVPP	s	0.010 872	E
		p	0.009 000	E
		d	0.003 000	
		d	0.001 000	
Be	TZ.3P	s	0.023 096	E
		p	0.016 372	E
		d	0.510 000	Ref. 63
		d	0.127 500	Ref. 63
Mg	TZVDP	s	0.013 457	E
		p	0.015 285	E
		d	0.350 000	Ref. 63
		d	0.087 500	Ref. 63
Sc	TZVDP	s	0.011 775	E
		p	0.010 730	E
		d	0.040 981	E
		f	0.350 000	
		f	0.090 000	
		g	0.100 000	
Cu	TZVP	s	0.013 896	E
		p	0.032 555	E
		d	0.084 703	E
		f	0.600 000	
		f	0.200 000	
		g	0.400 000	

dard TURBOMOLE basis sets with diffuse and polarization functions. The resulting basis sets are listed in Table IV.

V. RESULTS

A. Choice of the test set

Compared to ground states, the amount of accurate experimental data on excited states in the literature is very limited, especially for polyatomic molecules. The choice of molecules for the test set was therefore mainly dictated by the availability of (presumably) accurate results from gas-phase experiments. Moreover, the test set was designed to contain a variety of excited states of different character and spin multiplicity. The set thus should be considered a collection of interesting examples. Although tempting, a statistical analysis does not make sense, because errors are of very different origin and show systematic behavior. We have observed that, by adding or removing a few cases, the outcome of a statistics can be changed rather arbitrarily. Moreover, a statistical analysis does not reflect the different quality of errors; for example, a systematic overestimation of element–hydrogen bond lengths is much less severe in practice than a failure to describe the strong C–O bond elongation in carbonyls upon $n-\pi^*$ excitation. For these reasons, we do not give any sta-

tistical data in the following, except for maximum deviations from experiment, indicated by bold typeface in Tables V–VIII.

We do not want to conceal that for certain manifest multireference cases, such as the 1^2B_2 state of NO_2 , all methods studied here exhibit instabilities of the reference state.^{47,48} This means that the ground state intersects with an excited state of different symmetry, usually during geometry optimization. As a consequence, negative or imaginary excitation energies occur, and the response formalism breaks down.²² Another well-known example is the singlet ground state of the C_2 molecule, which is triplet unstable in HF and DFT methods even at the ground state geometry. An adequate treatment of these difficult systems remains the domain of multideterminantal methods.

B. Adiabatic excitation energies

Adiabatic excitation energies are in general more difficult to calculate than vertical ones because they require a theoretical model to work well not only at the equilibrium structure of the ground state but also of the excited state. Obviously, the CIS and TDHF results in Table V depend sensitively on the quality of the HF reference determinant in the *excited* state structure. In cases such as the $1^1\Pi$ states of CO and SiO, the 2^1B_1 state of H_2O , the $1^1A''$ state of CH_2O , or the 1^1B_{2u} state of C_6H_6 , the structure changes little upon excitation, and the HF reference is reasonable for both ground and excited states. Thus, as expected from variational considerations, CIS adiabatic excitation energies are 1–2 eV too high, which is somewhat improved by TDHF. On the other hand, for the $1^1\Sigma^-$ state of N_2 , the $1^1A''$ state of HCN, or the 1^1A_u state of C_2H_2 , the CIS adiabatic excitation energies are too small by about 1 eV, indicating multireference ground states at the excited state structure. TDHF fails even more badly due to nonreal instabilities leading to imaginary excitation energies for excited singlet states of N_2 and C_2H_2 . Nonreal instabilities of the HF reference are not uncommon for geometries differing significantly from that of the ground state, while for triplet states TDHF stability problems often occur for vertical excitations already. This lack of stability makes TDHF rather useless as a method for the investigation of excited potential energy surfaces.

Absolute errors in the LDA and GGA adiabatic excitation energies are considerably smaller and more systematic than those found for CIS and TDHF. For example, LDA as well as the BP86 and PBE GGAs give a correct ordering of the three lowest singlet excited states of N_2 despite the different structure and character of these states. Even for the difficult cases HCN and C_2H_2 , comparably small errors of -0.4 or -0.5 eV are observed. This can be attributed to the fact that the ground state KS solution is stable on a much larger region of the potential energy surface than the HF solution.⁴⁸ The errors in the LDA and GGA adiabatic excitation energies follow a very similar pattern as those observed in vertical excitation energies for these methods. There is a tendency to underestimate excitation energies systematically, which increases as the KS ionization threshold is reached. Excitation energies of Rydberg states such as 2^1B_1 in H_2O are calculated too small, and may become even smaller if the

basis set is further augmented by diffuse functions. In the LDA and GGA treatments, 2^1B_1 of H_2O is a continuum state, which is clearly unphysical; these problems are well known from vertical excitation energy calculations, and various remedies have been suggested.^{49,50} Hybrid functionals perform significantly better for diffuse states, which is also not unexpected.⁵¹ As for vertical excitations, gradient corrections do not improve upon the LDA adiabatic excitation energies in general. The hybrid results mostly interpolate between TDHF and the GGA excitation energies. Error compensation therefore is observed only if GGA excitation energies are somewhat too small, and the TDHF values are too large. In all other situations, the admixture of HF exchange does not improve the GGA results. This is especially true for states where TDHF exhibits instabilities. The TDA scheme¹¹ can be expected to be more robust, in particular for triplet states, whose excitation energy is often severely underestimated by TDDFT methods; its performance in predicting adiabatic excitation energies may deserve further attention. Considering the present results, we hesitate to recommend hybrid functionals as the first choice in excited state calculations, since it appears to be difficult to decide *a priori* whether error compensation works for a particular state or not.

C. Structures, dipole moments, and vibrational frequencies

Relative errors in computed excited state structures, dipole moments, and vibrational frequencies are for all methods much smaller than errors in the excitation energies, as can be seen from Tables VI–VIII. In fact, the accuracy is often comparable to that of the corresponding ground state methods, as long as no stability problems occur. CIS bond lengths are in general several pm too small, and vibrational frequencies are too high by 20% and more, error characteristics well known from HF ground state calculations. One might conclude that CIS is already a useful method for the investigation of excited states. There are drawbacks, however. CIS apparently tends to an artificial symmetry breaking in delocalized systems such as the 1^1B_2 state of pyridine,⁵ as is also familiar from ground state HF. The CIS geometry is qualitatively in error for the $1^3A''$ state of CH_2S , which is predicted planar. The C–O stretching mode ν_2 in the $n-\pi^*$ excited carbonyl compounds CH_2O and $(\text{CHO})_2$ is 400–600 cm^{-1} too high in the CIS treatment, and C–O bond lengths are too small. TDHF is not reliable due to stability problems and hardly improves upon CIS even for stable systems.

All density functional methods yield substantially better results for excited state structures, dipole moments, and vibrational frequencies than CIS. As for ground states, bond lengths are somewhat overestimated by GGA functionals; the LDA and hybrid functionals give slightly shorter bonds. Nevertheless, the GGA errors are systematic, and the general picture obtained from GGA calculations is very consistent. For example, the elongation of the C–O bond upon excitation in CH_2O and $(\text{CHO})_2$ is best described by the GGA, and the same trend is observed for other excitations with considerable changes in the bond order. The accuracy of the calcu-

TABLE V. Calculated adiabatic excitation energies (eV) compared to experiment. Calculated and experimental energies include ZPE differences (T_0 values) except for diatomics and porphyrin (T_e values). Experimental results are from Ref. 64 for diatomic and from Ref. 65 for polyatomic molecules, unless otherwise stated. Instabilities of the reference state are denoted by (I); bold typeface indicates maximum absolute deviations from experiment. RPA stands for TDHF, LDA for PW, BLP for BLYP, BP for BP86, PB0 for PBE0 and B3P for B3LYP.

System	State	CIS	RPA	LDA	BLP	BP	PBE	PB0	B3P	Expt.
BeH	1 $^2\Pi$	2.72	2.69	2.35	2.53	2.51	2.49	2.52	2.55	2.48
Li ₂	1 $^1\Sigma_u^+$	2.12	1.96	1.91	1.92	1.88	1.91	1.95	1.95	1.74
BH	1 $^1\Pi$	2.85	2.64	2.49	2.71	2.72	2.66	2.64	2.68	2.87
NH	1 $^3\Pi$	4.18	4.02	3.63	3.91	4.02	3.98	3.96	3.87	3.70
BeO	1 $^1\Pi$	2.37	2.27	1.26	1.05	1.21	1.15	1.44	1.26	1.17
BF	1 $^1\Pi$	6.55	6.22	5.95	5.99	6.04	6.02	6.12	6.08	6.34
N ₂	1 $^3\Pi_g$	7.70	7.20	7.03	6.76	6.73	6.74	6.96	6.98	7.39
	1 $^1\Sigma_u^+$	7.54	(I)	8.27	7.99	8.09	8.10	7.95	7.90	8.45
	1 $^1\Pi_g$	9.60	9.27	8.46	8.34	8.39	8.39	8.69	8.61	8.59
	1 $^1\Delta_u$	8.12	7.59	8.86	8.32	8.50	8.55	8.55	8.36	8.94
CO	1 $^3\Pi$	5.77	5.13	5.73	5.49	5.40	5.43	5.49	5.59	6.04
	1 $^1\Pi$	8.81	8.50	7.84	7.79	7.83	7.82	8.06	8.00	8.07
NO	1 $^2\Sigma^+$	(I)	(I)	(I)	5.50	5.75	5.45	6.22	6.09	5.45
Mg ₂	1 $^1\Sigma_u^+$	3.33	3.23	3.20	3.21	3.20	3.16	3.17	3.24	3.23
SiO	1 $^1\Pi$	6.11	5.87	5.06	4.93	4.98	4.97	5.25	5.17	5.31
ScO	1 $^2\Pi$	2.00	1.94	2.00	1.94	1.93	1.86	1.87	1.95	2.04 ^a
CuH	2 $^1\Sigma^+$	3.93	3.84	3.06	2.85	2.97	2.91	3.09	2.99	2.91
H ₂ O	2 1B_1	11.73	11.70	9.01	8.70	8.84	8.88	9.82	9.50	10.00
PH ₂	1 2A_1	2.78	2.59	2.13	2.34	2.40	2.38	2.40	2.34	2.27
SO ₂	1 3B_1	3.01	(I)	2.73	2.43	2.43	2.45	2.51	2.54	3.19
SiF ₂	1 1B_1	5.91	5.58	5.15	5.11	5.11	5.09	5.29	5.29	5.34
CCl ₂	1 1B_1	2.17	(I)	(I)	2.04	2.00	1.96	(I)	1.94	2.14 ^b
CS ₂	1 3A_2	3.37	(I)	3.23	2.98	3.02	3.05	3.04	3.01	3.25
HCN	1 $^1A''$	5.64	4.88	6.27	5.97	6.07	6.09	6.03	5.96	6.48
HCP	1 $^1A''$	3.55	(I)	4.08	3.86	3.95	3.96	3.88	3.82	4.31
C ₂ H ₂	1 1A_u	4.52	(I)	4.98	4.69	4.77	4.79	4.77	4.69	5.23
CH ₂ O ^c	1 $^1A''$	4.44	4.25	3.38	3.41	3.44	3.42	3.64	3.60	3.49
	1 $^3A''$	3.53	(I)	2.68	2.57	2.54	2.53	2.70	2.73	3.12
CH ₂ S ^c	1 1A_2	2.61	2.50	1.94	1.94	1.98	1.97	2.11	2.07	2.03
	1 $^3A''$	1.88	(I)	1.44	1.36	1.34	1.35	1.43	1.45	1.80
<i>trans</i> -(CHO) ₂	1 1A_u	3.59	3.41	1.90	2.04	2.01	1.98	2.45	2.42	2.72
Benzene ^d	1 $^1B_{2u}$	5.87	5.67	5.01	4.84	4.91	4.91	5.24	5.13	4.72 ^e
Pyridine ^f	1 1B_2	5.89 ^g	5.57 ^g	5.11 ^g	4.94	5.00	5.01	5.36	5.24	4.76 ^h
Porphyrin	1 $^1B_{1u}$	2.45	1.76	2.19	2.08	2.11	2.12	2.31	2.25	2.02 ⁱ

^aReference 66.

^bReference 67.

^cExperimental data from Ref. 68.

^dZPE calculated in the aug-SVP basis.

^eReference 69.

^fStructures and ZPE calculated in the SVP basis.

^gSaddle point.

^hReference 70.

ⁱ T_e value obtained by correction of experimental T_0 value (Ref. 71) by ZPE difference calculated using B3LYP/SVP.

TABLE VI. Calculated excited state equilibrium structures compared to experiment (bond lengths in pm, angles in degrees). Experimental r_e values are corrected for anharmonicity. See Table V for further explanations.

System	State	Param.	CIS	RPA	LDA	BLP	BP	PBE	PB0	B3P	Expt.
BeH	$1^2\Pi$	r_e	132	132	134	133	133	134	133	132	133
Li ₂	$1^1\Sigma_u^+$	r_e	309	320	307	307	307	307	307	307	311
BH	$1^1\Pi$	r_e	120	120	123	121	122	123	121	121	122
NH	$1^3\Pi$	r_e	102	101	106	106	105	105	104	104	104
BeO	$1^1\Pi$	r_e	142	144	143	143	145	144	143	143	146
BF	$1^1\Pi$	r_e	129	129	129	130	130	130	130	130	130
N ₂	$1^3\Pi_g$	r_e	118	119	120	121	121	121	120	120	121
	$1^1\Sigma_u^+$	r_e	126	(I)	127	129	129	129	128	128	128
	$1^1\Pi_g$	r_e	119	120	121	122	122	122	121	121	122
	$1^1\Delta_u$	r_e	123	126	127	129	129	128	126	127	127
CO	$1^3\Pi$	r_e	118	119	120	121	121	121	120	120	121
	$1^1\Pi$	r_e	121	122	122	124	124	123	122	123	124
NO	$1^2\Sigma^+$	r_e	(I)	(I)	(I)	107	107	107	105	105	106
Mg ₂	$1^1\Sigma_u^+$	r_e	324	321	309	317	319	316	316	316	308
SiO	$1^1\Pi$	r_e	158	159	160	163	162	162	161	162	162
ScO	$1^2\Pi$	r_e	166	166	168	172	171	170	168	170	169 ^a
CuH	$2^1\Sigma^+$	r_e	151	150	159	163	162	162	157	158	157
H ₂ O	2^1B_1	O–H	96	96	102	102	102	101	100	100	102
		$\angle(\text{HOH})$	109	109	105	104	105	104	105	105	107
PH ₂	1^2A_1	P–H	139	139	141	141	141	141	140	140	140
		$\angle(\text{HPH})$	120	121	123	122	122	122	122	122	123
SO ₂	1^3B_1	S–O	144	(I)	151	154	153	153	150	151	149
		$\angle(\text{OSO})$	127	(I)	126	125	126	126	127	126	126
SiF ₂ ^b	1^1B_1	Si–F	158	158	163	167	166	166	162	163	160
		$\angle(\text{FSiF})$	111	112	114	114	114	114	114	114	116
CCl ₂ ^b	1^1B_1	C–Cl	165	(I)	(I)	167	166	165	(I)	165	165
		$\angle(\text{ClCCl})$	133	(I)	(I)	134	135	135	(I)	135	131
CS ₂	1^3A_2	C–S	159	(I)	163	165	164	164	162	163	164
		$\angle(\text{SCS})$	145	(I)	138	137	137	137	138	138	136
HCN	$1^1A''$	C–H	110	108	115	114	114	114	112	112	114
		N–C	128	135	129	130	130	130	129	130	130
		$\angle(\text{HCN})$	121	125	123	123	123	123	123	123	125
HCP	$1^1A''$	P–C	168	(I)	169	172	171	171	170	170	169
		$\angle(\text{HCP})$	132	(I)	129	127	127	128	130	129	128
C ₂ H ₂	1^1A_u	C–C	135	(I)	136	137	137	137	136	137	139
		$\angle(\text{HCC})$	125	(I)	124	122	122	122	122	123	120
CH ₂ O ^c	$1^1A''$	C–H	109	109	111	110	110	110	110	109	110
		C–O	125	125	128	131	131	131	128	129	132
		$\angle(\text{HCH})$	118	117	115	117	116	116	116	117	118
	ϕ	22	24	34	31	33	33	31	30	34	
	$1^3A''$	C–H	109	(I)	112	111	110	111	111	110	108
		C–O	124	(I)	128	132	131	131	128	129	131
$\angle(\text{HCH})$		112	(I)	111	112	110	111	110	112	122	
ϕ	40	(I)	44	46	49	48	47	45	41		
CH ₂ S ^c	1^1A_2	C–H	107	107	109	109	109	109	108	108	108
		C–S	163	163	168	171	170	170	167	168	168
		$\angle(\text{HCH})$	119	118	120	120	120	120	119	119	121
	$1^3A''$	C–H	107	(I)	109	109	109	109	108	108	108
		C–S	162	(I)	167	171	170	170	167	168	168
		$\angle(\text{HCH})$	119	(I)	120	119	118	118	119	119	119

TABLE VI. (Continued.)

System	State	Param.	CIS	RPA	LDA	BLP	BP	PBE	PB0	B3P	Expt.	
		ϕ	0	(I)	1	22	26	24	18	15	12	
<i>trans</i> -(CHO) ₂ ^d	1 ¹ A _u	C–H	109	109	112	111	111	111	110	110	112	
		C–O	119	120	123	125	124	124	122	123	125	
		C–C	151	151	146	148	148	147	148	148	148	146
		\angle (HCC)	112	113	113	114	114	114	114	113	113	114
		\angle (OCC)	124	123	126	125	126	126	126	125	125	124
Benzene ^e	1 ¹ B _{2u}	C–H	107	107	109	109	109	109	108	108	108	
		C–C	141	141	142	143	143	143	143	142	142	143

^aReference 66.^bExperimental data from Ref. 67.^cExperimental data from Ref. 68.^dExperimental data from Ref. 72.^eExperimental data from Ref. 69.

lated excited state dipole moments is surprisingly high for both LDA and GGA, while hybrid functionals can suffer from artifacts of TDHF and do not always improve upon GGA. For vibrational frequencies of excited states, GGA functionals, especially BP86 and PBE, are superior to all other methods. Some caution is appropriate, however, since most experimental frequencies in Table VIII are not corrected for anharmonicity effects. Again, there is apparently no benefit from admixing HF exchange. The LDA frequencies tend to somewhat lower values. For example, the lowest b_1 mode of the 1 ¹B₂ state of pyridine is imaginary in the LDA, which is probably an artifact. On the other hand, the critical C–O stretching modes in the lowest singlet excited states of CH₂O and (CHO)₂ are calculated about 100 cm⁻¹ higher than within the GGA. However, even the GGA methods fail to give the correct ordering of the totally symmetric ν_2 and ν_3 modes. With a measured separation of only 100 and 200 cm⁻¹, the correct assignment of ν_2 and ν_3 is certainly a challenge. This example illustrates well the degree of accuracy that can be expected from TDDFT excited state calculations. In the vast majority of the vibrations in Table

VIII, the GGA assignment is correct, though. This is most important for the possible use of TDDFT in excited state structure elucidation, since vibrational frequencies are often the only structural information which is experimentally accessible in excited states of larger systems.

VI. CONCLUSIONS

Stability of the ground state is critical in single-reference treatments of excited state properties. TDDFT is considerably more robust than CIS and especially TDHF since the KS reference is stable on a larger range of nuclear geometries than the HF reference. TDDFT adiabatic excitation energies improve upon CIS and TDHF, but errors can reach 0.4 eV and more, which is still far from the desired “chemical accuracy” of 0.05 eV. However, TDDFT excited state structures, dipole moments, and force constants are nearly as accurate as the corresponding DFT ground state properties; similar behavior can be expected for activation barriers and reaction paths. In view of the success of ground state DFT, this is a promising result. With the availability of stable and efficient TDDFT implementations, CIS will become obsolete for excited state geometry optimizations since it generally leads to inferior results at the same computational cost. We recommend TDDFT for standard applications to excited states of molecules in the size range of 20–200 atoms, where correlated *ab initio* methods are still too expensive.

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APPENDIX A: DERIVATION OF THE EQUATIONS FOR THE LAGRANGE MULTIPLIERS Z AND W

In this Appendix, it is shown in detail how to derive the equations for the Lagrange multipliers Z and W in Sec. II C from the orbital stationarity condition (15). In order to trans-

TABLE VII. Calculated excited state dipole moments (*D*) compared to experiment. See Table V for further explanations.

System	State	CIS	RPA	LDA	BLP	BP	PBE	PB0	B3P	Expt.
BH	1 ¹ Π	0.63	0.48	0.51	0.44	0.52	0.49	0.49	0.49	0.58
NH	1 ³ Π	1.26	1.22	1.37	1.31	1.29	1.28	1.27	1.30	1.31
CO	1 ³ Π	2.14	2.52	1.24	1.36	1.34	1.30	1.58	1.57	1.37
	1 ¹ Π	1.08	1.08	0.29	0.26	0.25	0.23	0.50	0.49	0.34 ^a
NO	1 ² Σ ⁺	(I)	(I)	(I)	1.21	1.71	1.54	1.48	1.17	1.10
ScO	1 ² Π	4.96	5.09	4.36	4.69	4.34	4.33	4.54	4.88	4.14 ^b
CH ₂ O ^c	1 ¹ A''	1.37	1.28	1.63	1.56	1.56	1.54	1.51	1.53	1.57
	1 ³ A''	1.40	(I)	1.57	1.41	1.42	1.42	1.42	1.41	1.29
CH ₂ S ^c	1 ¹ A ₂	0.44	0.37	0.84	0.80	0.84	0.83	0.73	0.72	0.79
	1 ³ A''	0.02	(I)	0.56	0.50	0.56	0.55	0.41	0.38	0.57

^aReference 73.^bReference 66.^cExperimental data from Ref. 68.

TABLE VIII. Calculated harmonic vibrational frequencies (cm^{-1}) compared to experiment. Experimental ω_e values are corrected for anharmonicity. See Table V for further explanations.

System	State	Mode	CIS	RPA	LDA	BLP	BP	PBE	PB0	B3P	Expt.
BeH	$1^2\Pi$	ω_e	2241	2232	2083	2117	2096	2090	2150	2161	2089
Li ₂	$1^1\Sigma_u^+$	ω_e	271	235	249	243	256	253	258	248	255
BH	$1^1\Pi$	ω_e	2551	2602	2281	2306	2263	2267	2389	2406	2251
NH	$1^3\Pi$	ω_e	3594	3618	3015	2937	3000	3015	3219	3123	3231
BeO	$1^1\Pi$	ω_e	1254	1084	1250	1218	1210	1205	1219	1251	1144
BF	$1^1\Pi$	ω_e	1369	1368	1308	1227	1244	1244	1297	1274	1265
N ₂	$1^3\Pi_g$	ω_e	2027	1781	1858	1728	1767	1782	1840	1792	1733
	$1^1\Sigma_u^+$	ω_e	1686	(I)	1387	1282	1311	1318	1545	1513	1530
	$1^1\Pi_g$	ω_e	1904	1802	1789	1665	1707	1719	1789	1736	1694
	$1^1\Delta_u$	ω_e	1861	1496	1544	1457	1483	1488	1622	1576	1559
CO	$1^3\Pi$	ω_e	1963	1854	1831	1729	1762	1769	1836	1792	1743
	$1^1\Pi$	ω_e	1636	1584	1611	1474	1513	1524	1591	1543	1518
NO	$1^2\Sigma^+$	ω_e	(I)	(I)	(I)	2393	2397	2443	2574	2552	2374
Mg ₂	$1^1\Sigma_u^+$	ω_e	153	160	177	153	156	153	163	156	191
SiO	$1^1\Pi$	ω_e	944	907	1057	874	895	897	925	900	853
ScO	$1^2\Pi$	ω_e	973	967	865	809	837	845	891	846	876 ^a
CuH	$2^1\Sigma^+$	ω_e	1817	1811	1584	1588	1604	1611	1738	1711	1698
H ₂ O	2^1B_1	$\nu_1(a_1)$	3832	3834	2995	2978	2946	2997	3261	3213	3170
PH ₂	1^2A_1	$\nu_2(a_1)$	1046	1042	919	951	934	929	959	977	951
SO ₂	1^3B_1	$\nu_1(a_1)$	1157	(I)	935	763	881	888	973	928	906
		$\nu_2(a_1)$	454	(I)	353	338	341	342	368	361	360
		$\nu_2(a_1)$	866	870	702	623	648	646	744	715	598
SiF ₂	1^1B_1	$\nu_2(a_1)$	300	296	230	220	223	221	249	245	342
		$\nu_1(a_1)$	678	(I)	(I)	590	617	622	(I)	630	634
CCl ₂ ^b	1^1B_1	$\nu_2(a_1)$	311	(I)	(I)	280	273	260	(I)	272	303
		$\nu_1(a_1)$	716	(I)	716	665	681	686	705	689	692
CS ₂	1^3A_2	$\nu_2(a_1)$	279	(I)	309	305	306	305	296	303	311
		$\nu_1(a_1)$	629	425	950	973	969	964	983	992	941
HCN	$1^1A''$	$\nu_3(a')$	1766	1686	1532	1458	1477	1483	1557	1531	1496
		$\nu_2(a')$	588	(I)	668	708	699	690	668	694	567
HCP	$1^1A''$	$\nu_3(a')$	844	(I)	966	914	931	936	983	959	951
		$\nu_2(a')$	1549	(I)	1448	1389	1427	1403	1456	1437	1385
C ₂ H ₂	1^1A_u	$\nu_3(a_g)$	1149	(I)	1041	1084	1098	1078	1088	1097	1048
		$\nu_2(a_g)$	3135	3134	2871	2918	2906	2916	3002	2987	2846
CH ₂ O ^c	$1^1A''$	$\nu_2(a')$	1633	1620	1364	1279	1289	1294	1408	1361	1183
		$\nu_3(a')$	1385	1390	1194	1247	1249	1254	1287	1301	1293
		$\nu_5(a'')$	3223	3217	2963	3023	3008	3016	3096	3083	2968
		$\nu_6(a'')$	947	954	809	870	852	855	873	890	904
		$\nu_2(a')$	1613	(I)	1369	1201	1251	1261	1369	1323	1283
		$\nu_1(a')$	3265	3265	3050	3063	3066	3068	3148	3133	3034
CH ₂ S ^c	1^1A_2	$\nu_2(a_1)$	1488	1485	1293	1334	1329	1311	1365	1377	1316
		$\nu_3(a_1)$	1070	1071	904	835	862	870	942	903	820
		$\nu_5(b_2)$	3366	3364	3162	3176	3180	3183	3260	3242	3081
		$\nu_6(b_2)$	851	846	749	773	773	752	789	803	799
		$\nu_2(a')$	1482	(I)	1286	1329	1306	1303	1346	1364	1320
		$\nu_3(a')$	1096	(I)	912	836	858	868	948	909	859
<i>trans</i> -(CHO) ₂ ^d	1^1A_u	$\nu_1(a_g)$	3164	3177	2837	2888	2882	2883	2986	2965	2809
		$\nu_2(a_g)$	1806	1796	1589	1475	1513	1520	1622	1570	1391
		$\nu_3(a_g)$	1295	1305	1170	1222	1208	1204	1226	1237	1195

TABLE VIII. (Continued.)

System	State	Mode	CIS	RPA	LDA	BLP	BP	PBE	PB0	B3P	Expt.
		$\nu_4(a_g)$	1009	1017	987	957	970	973	991	972	952
		$\nu_5(a_g)$	544	544	512	509	508	509	521	520	509
		$\nu_6(a_u)$	838	838	757	761	763	759	796	786	720
		$\nu_7(a_u)$	256	256	258	249	253	252	267	259	233
		$\nu_8(b_g)$	859	856	767	765	765	764	797	789	735
		$\nu_{10}(b_u)$	1709	1682	1565	1460	1492	1499	1576	1530	1281
		$\nu_{11}(b_u)$	1326	1331	1093	1125	1112	1110	1197	1198	1172
		$\nu_{12}(b_u)$	441	441	337	344	341	341	397	392	379
Benzene ^e	1^1B_{2u}	$\nu_1(a_{1g})$	3392	3392	3146	3147	3155	3161	3252	3226	3093
		$\nu_2(a_{1g})$	1026	1025	965	928	939	943	981	963	923
		$\nu_3(a_{2g})$	1455	1452	1231	1286	1286	1275	1332	1331	1327
		$\nu_4(a_{2u})$	647	647	575	592	575	573	596	619	515-518
		$\nu_7(b_{2g})$	905	907	868	868	842	838	879	922	745
		$\nu_8(b_{2g})$	426	434	247	370	331	319	377	418	365
		$\nu_9(b_{2u})$	1849	1912	1458	1380	1408	1415	1532	1482	1571
		$\nu_{10}(b_{2u})$	1254	1254	1099	1126	1125	1119	1161	1160	1150
		$\nu_{11}(e_{1g})$	724	724	595	629	606	602	639	666	581
		$\nu_{12}(e_{1u})$	3381	3381	3137	3137	3145	3152	3242	3217	3084
		$\nu_{13}(e_{1u})$	1570	1570	1374	1386	1388	1383	1449	1440	1405
		$\nu_{14}(e_{1u})$	1062	1061	944	920	933	934	989	971	920
		$\nu_{15}(e_{2g})$	3367	3366	3125	3125	3132	3139	3229	3204	3077
		$\nu_{16}(e_{2g})$	1713	1714	1545	1501	1520	1523	1604	1570	1516
		$\nu_{17}(e_{2g})$	1249	1248	1112	1128	1132	1128	1169	1163	1148
		$\nu_{18}(e_{2g})$	571	560	495	512	507	506	523	525	521
		$\nu_{19}(e_{2u})$	887	888	798	797	781	779	820	843	717
		$\nu_{20}(e_{2u})$	269	286	262	275	272	267	292	304	238
Pyridine ^f	1^1B_2	$\nu_6(a_1)$	1309	1311	1172	1169	1173	1173	1221	1210	1215 ^g
		$\nu_8(a_1)$	1086	1089	971	939	950	954	1003	984	995
		$\nu_9(a_1)$	1049	1048	941	911	921	925	977	960	950 ^g
		$\nu_{10}(a_1)$	565	566	489	502	496	495	512	516	542
		$\nu_{13}(a_2)$	(im.)	(im.)	257	272	266	264	313	309	327 ^g

^aReference 66.^bExperimental data from Ref. 67.^cExperimental data from Ref. 68.^dExperimental data from Ref. 74.^eAug-SVP basis set, experimental data from Ref. 69.^fSVP basis.^gReference 70.

form Eq. (15) to a more manageable form, we multiply both sides by $C_{\mu q\sigma}$ and sum over μ . Using the definition of L (12), this leads to

$$\begin{aligned}
 Q_{pq\sigma} + \sum_{ia\sigma'} Z_{ia\sigma'} \sum_{\mu} \frac{\partial F_{ia\sigma'}}{\partial C_{\mu p\sigma}} C_{\mu q\sigma} \\
 = \sum_{rs\sigma', r \leq s} W_{rs\sigma'} \sum_{\mu} \frac{\partial S_{rs\sigma'}}{\partial C_{\mu p\sigma}} C_{\mu q\sigma}, \quad (\text{A1})
 \end{aligned}$$

where Q is given by

$$Q_{pq\sigma} = \sum_{\mu} \frac{\partial G[X, Y, \Omega]}{\partial C_{\mu p\sigma}} C_{\mu q\sigma}. \quad (\text{A2})$$

In the next step, we evaluate the derivatives with respect to C . This is conveniently done by expressing all operator matrix elements in terms of AO integrals, e.g.,

$$h_{pq\sigma} = \sum_{\mu\nu} C_{\mu p\sigma} h_{\mu\nu} C_{\nu q\sigma}. \quad (\text{A3})$$

If $p = i \leq q = j$ are both occupied, Eq. (A1) thus transforms to

$$Q_{ij\sigma} + H_{ij\sigma}^+[Z] = W_{ij\sigma}, \quad (\text{A4})$$

where H is defined in Eq. (20), and, using the unrelaxed difference density matrix T from Eq. (19),

$$\begin{aligned}
 Q_{ij\sigma} = \sum_a \Omega \{ (X+Y)_{ia\sigma} (X-Y)_{ja\sigma} (X-Y)_{ia\sigma} (X+Y)_{ja\sigma} \} \\
 - \sum_a \epsilon_{a\sigma} \{ (X+Y)_{ia\sigma} (X+Y)_{ja\sigma} \\
 + (X-Y)_{ia\sigma} (X-Y)_{ja\sigma} \} + H_{ij\sigma}^+[T] \\
 + 2 \sum_{kc\sigma' ld\sigma''} g_{ij\sigma kc\sigma' ld\sigma''}^{\text{xc}} (X+Y)_{kc\sigma'} (X+Y)_{ld\sigma''}. \quad (\text{A5})
 \end{aligned}$$

Here, the definition of G (1) has been inserted; moreover, the fact that the MO coefficients C satisfy the KS equations and the excitation vector solves the TDKS eigenvalue problem (6a) has been exploited, which is clearly legitimate after the derivative has been taken. Similarly, we obtain for the occ-virt block

$$Q_{ia\sigma} + \epsilon_{a\sigma} Z_{ia\sigma} + H_{ia\sigma}^+[Z] = W_{ia\sigma}, \quad (\text{A6})$$

$$Q_{ia\sigma} = \sum_b \{ (X+Y)_{ib\sigma} H_{ab\sigma}^+[X+Y] + (X-Y)_{ib\sigma} H_{ab\sigma}^-[X-Y] \} + H_{ia\sigma}^+[T] + 2 \sum_{jb\sigma'kc\sigma''} g_{ia\sigma jb\sigma'kc\sigma''}^{\text{xc}} (X+Y)_{jb\sigma'} (X+Y)_{kc\sigma''}, \quad (\text{A7})$$

for the virt-occ block

$$Q_{ai\sigma} + \epsilon_{i\sigma} Z_{ia\sigma} = W_{ia\sigma}, \quad (\text{A8})$$

$$Q_{ai\sigma} = \sum_j \{ (X+Y)_{ja\sigma} H_{ji\sigma}^+[X+Y] + (X-Y)_{ja\sigma} H_{ji\sigma}^-[X-Y] \}, \quad (\text{A9})$$

and for the virt-virt block, with $a \leq b$,

$$Q_{ab\sigma} = W_{ab\sigma}, \quad (\text{A10})$$

$$Q_{ab\sigma} = \sum_i \Omega \{ (X+Y)_{ia\sigma} (X-Y)_{ib\sigma} + (X-Y)_{ia\sigma} (X+Y)_{ib\sigma} \} + \sum_i \epsilon_{i\sigma} \{ (X+Y)_{ia\sigma} (X+Y)_{ib\sigma} + (X-Y)_{ia\sigma} (X-Y)_{ib\sigma} \}. \quad (\text{A11})$$

Subtracting Eq. (A8) from (A6), we obtain

$$(\epsilon_{a\sigma} - \epsilon_{i\sigma}) Z_{ia\sigma} + H_{ia\sigma}^+[Z] = -(Q_{ia\sigma} - Q_{ai\sigma}), \quad (\text{A12})$$

which is the Z vector equation (18) with the RHS given in Eq. (21). Once the Z vector equation has been solved, W is determined from Eqs. (A4), (A10), and the sum of Eqs. (A8) and (A6) according to

$$W_{ij\sigma} = Q_{ij\sigma} + H_{ij\sigma}^+[Z], \\ W_{ab\sigma} = Q_{ab\sigma}, \\ W_{ia\sigma} = Q_{ai\sigma} + \epsilon_{i\sigma} Z_{ia\sigma}. \quad (\text{A13})$$

This is identical to the definition of W as given in Eq. (24).

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