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An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules

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Time-dependent density-functional (TDDFT) methods are applied within the adiabatic approximation to a series of molecules including C_{70} . Our implementation provides an efficient approach for treating frequency-dependent response properties and electronic excitation spectra of large molecules. We also present a new algorithm for the diagonalization of large non-Hermitian matrices which is needed for hybrid functionals and is also faster than the widely used Davidson algorithm when employed for the Hermitian case appearing in excited energy calculations. Results for a few selected molecules using local, gradient-corrected, and hybrid functionals are discussed. We find that for molecules with low lying excited states TDDFT constitutes a considerable improvement over Hartree–Fock based methods (like the random phase approximation) which require comparable computational effort. © 1998 American Institute of Physics. [S0021-9606(98)30643-1]

I. INTRODUCTION

Time-dependent density-functional response theory (TD-DFT) has recently been reformulated (see, e.g., Refs. 1 and 2 for a review) to compute discrete transition energies and oscillator strengths and has been applied to a number of different atoms and molecules^{3–6}

In addition, given that the time-dependent Hartree–Fock (TDHF) scheme can be derived along the same lines as TDDFT, Bauernschmitt and Ahlrichs⁶ have also included the hybrid functionals proposed by Becke⁷ in the calculation of excitation energies. Based on a small set of benchmark molecules, they determined that the best results were obtained using the B3LYP functional.⁷ These hybrid methods typically constitute a considerable improvement over conventional Hartree–Fock (HF) based methods of comparable cost like the random phase approximation (RPA).

We next review some of the underlying theory with enough detail to document our implementation and to make the subsequent discussion self-contained. We then compare our implementation, which includes a new algorithm for obtaining the lowest few eigenvectors of large non-Hermitian matrices, to other algorithms. Finally, we present results for C_{70} , a large molecule of current interest, to demonstrate the feasibility of obtaining excitation energies for large systems with a number of theoretical methods.

II. THEORY

The formal foundations of TDDFT theory have been reviewed elsewhere by Gross and Kohn.⁸ For additional details, we refer the reader to the papers by Casida.^{1,2} As men-

tioned above, we here rederive the expressions previously presented by other authors^{1,2} giving only enough details to make the present paper self-contained and to document the working equations of our implementation. Note that when no confusion should arise, we do not include spin variables.

The time-dependent Kohn-Sham equation

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

can be derived assuming the existence of a potential $v_{\text{eff}}(\mathbf{r}, t)$, for an independent particle system, whose orbitals $\psi(\mathbf{r}, t)$ yield the same charge density $\rho(\mathbf{r}, t)$ as for the interacting system. This potential has the form

$$v_{\text{eff}}(\mathbf{r}, t) = v(t) + v_{\text{SCF}}(\mathbf{r}, t), \quad (2)$$

where $v(t)$ is an applied field (perturbation) turned on slowly in the distant past. The self-consistent field v_{SCF} is defined as

$$v_{\text{SCF}}(\mathbf{r}, t) = \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}, t), \quad (3)$$

where the exchange-correlation potential is given as the functional derivative of the exchange-correlation action A_{xc} , represented by

$$v_{\text{xc}}[\rho](\mathbf{r}, t) = \frac{\delta A_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r}, t)} \approx \frac{\delta E_{\text{xc}}[\rho_t]}{\delta \rho_t(\mathbf{r})} = v_{\text{xc}}[\rho_t](\mathbf{r}). \quad (4)$$

Here the unknown functional A_{xc} of ρ over both space and time is approximated by E_{xc} (the exchange-correlation functional of time-independent Kohn-Sham theory) which is a function ρ_t of space at fixed t . This local approximation in time is commonly referred to as the adiabatic approximation

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and appears to work best for low-lying excited states of clear valence type when used in conjunction with standard functionals.^{6,9}

A. Linear response of the density matrix

For a system initially in the ground state, the effect of a perturbation introduced into the Kohn-Sham (or the HF) Hamiltonian by turning on an applied field $\delta v(t)$ is, to first order

$$\delta v_{\text{eff}}(\mathbf{r}, t) = \delta v(t) + \delta v_{\text{SCF}}(\mathbf{r}, t), \quad (5)$$

where $\delta v_{\text{SCF}}(\mathbf{r}, t)$ is the linear response of the self-consistent field arising from the change in the charge density given by (transforming to the frequency representation)

$$\begin{aligned} \delta \rho(\mathbf{r}, \omega) = & \sum_{ai} \delta P_{ai}(\omega) \psi_a(\mathbf{r}) \psi_i^*(\mathbf{r}) \\ & + \sum_{ia} \delta P_{ia}(\omega) \psi_i(\mathbf{r}) \psi_a^*(\mathbf{r}) \end{aligned} \quad (6)$$

where $\delta P_{st}(\omega)$ is the linear response of the KS/HF density matrix in the basis of the unperturbed molecular orbitals. It is convenient to divide δP into hole-particle (δP_{ai}) and particle-hole (δP_{ia}) parts, which are related by complex conjugation, as these are the only nonzero terms. We use the usual convention in labeling the MOs (i.e., i, j for occupied; a, b for virtual; s, t, u, v for general orbitals). Using elementary results from time-dependent perturbation theory, one can write down the linear response of the KS/HF density matrix to the applied field as

$$\delta P_{st}(\omega) = \frac{\Delta n_{st}}{(\epsilon_s - \epsilon_t) - \omega} \delta v_{st}^{\text{eff}}(\omega), \quad (7)$$

where Δn_{st} is the difference in occupation numbers and is 1 for $st=ai$ and is -1 for $st=ia$. This last equation is somewhat more complicated due to the fact that the potential δv_{SCF} depends on the response of the density matrix

$$\begin{aligned} \delta v_{st}^{\text{SCF}}(\omega) = & \sum_{uv} K_{st,uv}(\omega) \delta P_{uv}(\omega) \\ = & \sum_{bj} K_{st,bj}(\omega) \delta P_{bj}(\omega) \\ & + \sum_{jb} K_{st,jb}(\omega) \delta P_{jb}(\omega), \end{aligned} \quad (8)$$

where the coupling matrix \mathbf{K} will be defined later. Substituting Eqs. (5) and (8) into Eq. (7) one obtains (after some algebra)

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - w \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \begin{pmatrix} \delta P \\ \delta P^* \end{pmatrix} = \begin{pmatrix} -\delta v \\ -\delta v^* \end{pmatrix}, \quad (9)$$

where the matrices \mathbf{A} and \mathbf{B} are defined as

$$A_{ai,bj} = \delta_{ab} \delta_{ij} (\epsilon_a - \epsilon_i) + K_{ai,bj} \quad (10)$$

and

$$B_{ai,bj} = K_{ai,jb}. \quad (11)$$

It should be noted that the last two indices on the coupling matrix \mathbf{K} are switched in the definitions of the \mathbf{A} and \mathbf{B} matrices.

B. Excitation energies in TDHF and TDDFT

The coupling matrix given above for TDDFT is easily determined using the chain rule and making use of Eqs. (3), (4) and (6). It is given by (were σ and τ are spin indices)

$$\begin{aligned} K_{st\sigma,uv\tau} = & \frac{\partial v_{st}^{\text{SCF}}}{\partial P_{uv}} \\ = & \frac{\partial v_{st}^{\text{Coul}}}{\partial P_{uv}} + \frac{\partial v_{st}^{\text{xc}}}{\partial P_{uv}} \\ = & (\psi_{s\sigma}^*(\mathbf{r}) \psi_{t\sigma}(\mathbf{r}) | \psi_{v\tau}^*(\mathbf{r}') \psi_{u\tau}(\mathbf{r}')) \\ & + \int d\mathbf{r} d\mathbf{r}' \psi_{s\sigma}^*(\mathbf{r}) \psi_{t\sigma}(\mathbf{r}) \frac{\delta^2 E_{\text{xc}}}{\delta \rho_{\sigma}(\mathbf{r}) \delta \rho_{\tau}(\mathbf{r}')} \\ & \times \psi_{v\tau}^*(\mathbf{r}') \psi_{u\tau}(\mathbf{r}'). \end{aligned} \quad (12)$$

Thus in the adiabatic approximation the coupling matrix is independent of ω (time and frequency independent) and is real when the molecular orbitals (MOs) are real. Explicit expressions for hybrid functionals have been published elsewhere.⁶ The time-dependent Hartree-Fock equations, also known as the random phase approximation, can be derived along the same lines as done here; the only difference with TDDFT is in this last equation which is

$$\begin{aligned} K_{st\sigma,uv\tau} = & (\psi_{s\sigma}^*(\mathbf{r}) \psi_{t\sigma}(\mathbf{r}) | \psi_{v\tau}^*(\mathbf{r}') \psi_{u\tau}(\mathbf{r}')) \\ & - (\psi_{s\sigma}^*(\mathbf{r}) \psi_{u\tau}(\mathbf{r}) | \psi_{v\tau}^*(\mathbf{r}') \psi_{t\sigma}(\mathbf{r}')). \end{aligned} \quad (13)$$

For RPA then, the \mathbf{A} matrix is just the CIS Hamiltonian (i.e., configuration interaction restricted to single excitations; see Ref. 10 for a review). In the notation used here, the interpretation of the \mathbf{B} matrix is clear; it involves both excitation and de-excitation elements. To be explicit, one considers an initially mono-excited state containing the orbitals $\psi_i \psi_j \psi_a \psi_b$, with orbitals ψ_i and ψ_b occupied and orbitals ψ_j and ψ_a vacant; this is the effect of swapping the indices in Eq. (11). The required matrix elements are then determined by considering the matrix elements of $\langle \psi(a \leftarrow i) | H | \psi(j \leftarrow b) \rangle$. Mathematically, this is also identical to computing matrix elements between doubly excited states and the ground state. Thus we see that RPA includes higher order correlation effects through double excitations that are not being accounted for in the configuration interaction singles (CIS) method. TDDFT includes additional correlation effects through the exchange-correlation potential. It should also be noticed that in the static limit ($\omega=0$), TDDFT becomes the coupled-perturbed Kohn-Sham (CPKS) approach.¹¹ This is of course true only in the adiabatic approximation.

In the case of TDDFT with real orbitals, $K_{st\sigma,uv\tau} = K_{st\sigma,uv\tau}$. This exchange of indices is not valid for the exchange portion in the RPA case. The higher degree of symmetry in the TDDFT case is due to the fact that the Kohn-Sham Hamiltonian only contains local potentials. Note that, if the linear combination $\mathbf{A} - \mathbf{B}$ is desired, it will lead to

a diagonal form in the case of TDDFT, and not so for the RPA case, which will include only exchange terms.

C. Working equations for TDHF and TDDFT

In response theory, excitation energies are determined as poles of the response functions, leading to zero eigenvalues on the left hand side of Eq. (9). They can thus be determined as solutions to the non-Hermitian eigenvalue problem

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = w \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}, \quad (14)$$

where the usual notation $X_{ai} = \delta P_{ai}(\omega)$ and $Y_{ia} = \delta P_{ia}(\omega)$ has been adopted. This eigenvalue problem, which is of dimension $2N$ (where $N = N_{\text{occ}} N_{\text{vir}}$), can be rewritten as a non-Hermitian problem of half the dimension (by means of a 2×2 unitary transformation)¹²

$$(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})|\mathbf{X} + \mathbf{Y}\rangle = w^2|\mathbf{X} + \mathbf{Y}\rangle, \quad (15)$$

where $\mathbf{A} + \mathbf{B}$ and $\mathbf{A} - \mathbf{B}$ do not commute. If $(\mathbf{A} - \mathbf{B})$ is positive definite this last equation can be further transformed [multiplying both sides on the left by $(\mathbf{A} - \mathbf{B})^{-1/2}$]

$$(\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2}\mathbf{T} = w^2\mathbf{T} \quad (16)$$

which is in the form of a Hermitian eigenvalue problem and where

$$\mathbf{T} = (\mathbf{A} - \mathbf{B})^{-1/2}|\mathbf{X} + \mathbf{Y}\rangle. \quad (17)$$

We note that in Eqs. (15) and (16), the \mathbf{A} and \mathbf{B} matrices appear as linear combinations of each other. As will be shown below, only matrix times vector products are of any interest, as dictated by the Davidson algorithm.¹³ The evaluation of these matrices times vector products can be done in a direct fashion (in the usual sense, so that the matrices are never constructed in memory). Additional details have been published elsewhere.¹⁴ To illustrate the efficiency of this procedure, we point out that the CIS matrix is usually computed as $\mathbf{A} = 1/2[(\mathbf{A} + \mathbf{B}) + (\mathbf{A} - \mathbf{B})]$.

We present two additional useful identities that are readily obtained from the above equations

$$(\mathbf{A} + \mathbf{B})|\mathbf{X} + \mathbf{Y}\rangle = w|\mathbf{X} - \mathbf{Y}\rangle \quad (18)$$

and

$$(\mathbf{A} - \mathbf{B})|\mathbf{X} - \mathbf{Y}\rangle = w|\mathbf{X} + \mathbf{Y}\rangle. \quad (19)$$

The vectors $|\mathbf{L}_i^{\text{True}}\rangle = |\mathbf{X} - \mathbf{Y}\rangle_i$ and $|\mathbf{R}_i^{\text{True}}\rangle = |\mathbf{X} + \mathbf{Y}\rangle_i$ are the respective left and right eigenvectors of the matrix product defined on the left hand side of Eq. (15). The normalization imposed on these vectors is given by the usual bi-orthogonality condition for non-Hermitian matrices

$$\langle |\mathbf{X} - \mathbf{Y}\rangle_i^* , |\mathbf{X} + \mathbf{Y}\rangle_j \rangle = \delta_{i,j}. \quad (20)$$

D. A new algorithm for large non-Hermitian matrix diagonalization

To determine excitation energies, it becomes necessary to solve one of the equation sets presented above. Different methods have been proposed to solve the time-dependent problem based on Eqs. (14), (15) and (16). For problems that are small enough, the simplest way to proceed consists in

solving Eq. (16); for obvious reasons, this is not practical for large dimensional problems unless $\mathbf{A} - \mathbf{B}$ happens to be diagonal (as discussed in the next section).

The first practical approach to solve the RPA equations for large cases was given by Rettrup¹⁵ who proposed to employ the Davidson algorithm to solve Eq. (15). The only required modification is (essentially) the diagonalization of a small reduced non-Hermitian matrix. This approach, advocated by Bouman *et al.*,¹⁶ works well in practice, but has been shown to take many iteration steps to converge.¹⁷

A much more efficient method proposed by Olsen *et al.*¹⁷ is based on projecting the large dimensional equation given in (14) into a subspace via paired expansion vectors. The resulting small dimensional problem can then be solved in a straightforward manner, and one iterates in a Davidson-like manner until convergence is achieved. This algorithm has been shown to converge much faster than the Rettrup¹⁵ algorithm and furthermore shows monotonic convergence.¹⁷

We now proceed to present our own implementation. For the sake of clarity, we present this approach in an algorithmic fashion. It is closely related to the Davidson algorithm¹³ for determining the lowest few eigenvalues and eigenvectors of a large Hermitian matrix.

Step 1. If the first k eigenvalues of the large N -dimensional problem are desired, select a zeroth-order orthonormal subspace, $\mathbf{b}_1, \mathbf{b}_2, \dots, \mathbf{b}_l$ ($l > k$) spanning the dominant (left and right) components of the first k eigenvectors.

Step 2. Form and save $\{(\mathbf{A} + \mathbf{B})\mathbf{b}_i, (\mathbf{A} - \mathbf{B})\mathbf{b}_i; i = 1, \dots, l\}$. This step is (by far) the most CPU intensive step.

Step 3. Form $\tilde{M}_{ij}^+ = (\mathbf{b}_i, (\mathbf{A} + \mathbf{B})\mathbf{b}_j)$, and $\tilde{M}_{ij}^- = (\mathbf{b}_i, (\mathbf{A} - \mathbf{B})\mathbf{b}_j)$, for $i, j = 1, \dots, l$. The tilde superscript has been added to indicate reduced matrices (i.e., of much smaller dimension $l \ll N$)

Step 4. Form the non-Hermitian matrix product

$$\tilde{M}_{ij}^{nh} = \sum_j \tilde{M}_{ij}^- \tilde{M}_{jk}^+ \quad (21)$$

which is the reduced analog of Eq. (15) to be diagonalized in the next step to obtain both left and right eigenvalues and eigenvectors. At first glance, the current approach might seem a little surprising. In view of Eq. (15), one would assume that the required reduced matrix should be (as required by the Rettrup algorithm)

$$\langle \mathbf{b}_i | (\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B}) | \mathbf{b}_j \rangle. \quad (22)$$

Thus the matrix product in Eq. (21) is clearly not a faithful matrix representation of the matrix given in Eq. (22). However, assuming that the k true left and right eigenvectors can be determined, it is clear that in this limit the two matrices are identical. This is easily verified by considering the matrix

$$\langle \mathbf{L} | \mathbf{A} - \mathbf{B} | \mathbf{L} \rangle \langle \mathbf{R} | \mathbf{A} + \mathbf{B} | \mathbf{R} \rangle \quad (23)$$

and using Eqs. (18), (19) and (20). In the reduced subspace that we are considering, instead of working with Eq. (21) we may alternatively (and prefer to) work with the reduced Hermitian analog of Eq. (16), using the matrices determined in Step 3:

TABLE I. Comparison of the convergence characteristics of the non-Hermitian algorithm presented in this paper with that of Olsen *et al.* (Ref. 17). Shown here is a case study of the six lowest lying singlet states of formaldehyde in a distorted geometry (see text). All entries are in eV and are relative to the final converged excitation energies. The numbers in parenthesis indicate the total number of expansion vectors used.

Iteration	Root					
	1	2	3	4	5	6
	This work					
1(24)	0.288 463 8	0.114 465 3	0.639 932 9	0.494 245 1	0.417 639 7	0.473 805 1
2(36)	0.002 096 9	0.003 347 1	0.172 616 3	0.158 678 5	0.004 410 2	0.105 542 5
3(48)	0.000 008 8	0.000 114 4	0.010 321 5	0.000 333 6	0.000 142 2	0.001 917 6
4(60)	0.000 000 1	0.000 002 3	0.000 325 0	0.000 008 1	0.000 004 6	0.000 060 1
5(72)			0.000 006 3	0.000 000 1	0.000 000 1	0.000 001 2
6(80)			0.000 001 8			0.000 000 5
	Iterative RPA method of Olsen <i>et al.</i> (Ref. 17)					
1(24)	0.377 197 6	0.030 576 6	0.552 762 4	0.478 243 3	0.255 423 6	0.241 295 3
2(36)	0.005 379 6	0.000 773 0	0.139 033 5	0.014 046 1	0.002 114 9	0.007 403 6
3(48)	0.000 059 6	0.000 048 9	0.005 279 7	0.000 640 3	0.000 218 3	0.000 439 7
4(60)	0.000 000 8	0.000 001 3	0.000 095 7	0.000 045 7	0.000 011 2	0.000 007 9
5(72)			0.000 003 0	0.000 003 0	0.000 000 3	0.000 000 3

$$\tilde{M}_{im}^h = \sum_{j,k} (\tilde{M}^-)^{1/2}_{ij} (\tilde{M}^+)^{1/2}_{jk} (\tilde{M}^-)^{1/2}_{km} \quad (24)$$

from which the left and right eigenvectors can be obtained. From this equation we can immediately see the convergence properties of the algorithm. Since McDonalds theorem applies here, we observe a monotonic convergence of the reduced eigenvalues.

Step 5. Diagonalize the reduced matrix given by Eq. (24) using a standard method for small matrices, and obtain the reduced eigenvalues $\tilde{\omega}_n$ (the best guess of the true n th eigenvalue) and left (\tilde{L}_n) and right (\tilde{R}_n) eigenvectors. The best approximation to the true N -dimensional right and left eigenvectors is then given by

$$|\mathbf{L}_n\rangle = \sum_{i=1}^l \tilde{L}_{in} |\mathbf{b}_i\rangle \quad (25)$$

and

$$|\mathbf{R}_n\rangle = \sum_{i=1}^l \tilde{R}_{in} |\mathbf{b}_i\rangle. \quad (26)$$

In the notation employed here, as we approach a large number of orthogonal expansion vectors, $|\mathbf{R}\rangle_n \rightarrow |\mathbf{X} + \mathbf{Y}\rangle_n$ and $|\mathbf{L}\rangle_n \rightarrow |\mathbf{X} - \mathbf{Y}\rangle_n$. Having obtained both left and right N -dimensional approximate eigenvectors we next impose the bi-orthogonality condition given in Eq. (20).

Step 6. In order to extend the dimensionality of the subspace, V_l , we must add a new and ‘‘optimal’’ set of vectors. We propose here to augment the subspace with $2k$ vectors. We can do this because we have a way of ‘‘guessing’’ which are missing left and right components. Thus we define the residual vectors \mathbf{W}_n as

$$\mathbf{W}_n^L = (\mathbf{A} + \mathbf{B})|\mathbf{R}_n\rangle - \tilde{\omega}_n |\mathbf{L}_n\rangle \quad (27)$$

and

$$\mathbf{W}_n^R = (\mathbf{A} - \mathbf{B})|\mathbf{L}_n\rangle - \tilde{\omega}_n |\mathbf{R}_n\rangle. \quad (28)$$

The residual vectors will vanish as we achieve convergence in view of Eqs. (18) and (19). Thus when the norms of the residual vectors falls below a pre-determined threshold, convergence is achieved and the algorithm is stopped. Following Davidson,¹³ we next define a set of perturbed \mathbf{Q}_n vectors as follows

$$\mathbf{Q}_{in} = (\tilde{\omega}_n - D_i)^{-1} \mathbf{W}_{in}, \quad i = 1, \dots, N, \quad (29)$$

where D_i are approximate diagonal elements of the non-Hermitian matrix to be diagonalized which we take to be $\epsilon_a - \epsilon_i$ [see Eq. (10)].

Step 7. Orthonormalize the current \mathbf{Q}_n vectors amongst themselves and with respect to the previous l expansion vectors. Include these new vectors in the expansion set. Form and save $\{(\mathbf{A} + \mathbf{B})\mathbf{b}_i, (\mathbf{A} - \mathbf{B})\mathbf{b}_i; i = l+1, \dots, l+2k\}$. Set l equal to $l+2k$. Go to Step 3.

E. Convergence properties of the new algorithm

We illustrate in Table I the convergence characteristics of our algorithm, which we have implemented in the Gaussian suite of programs,¹⁸ and compared it to the algorithm of Olsen *et al.*¹⁷ as implemented in the RPAC program.¹⁶ Here we considered the six lowest singlet roots of formaldehyde at the 6-31G+G*/RPA level of theory with all electrons active. The (distorted) geometry we employed for this molecule is as follows: C_{2v} symmetry; C–O bond length of 1.22 Å, C–H bond length of 1.08 Å, and all interior angles of 120°. This geometry leads to all positive roots for triplet excitations.

The first column in Table I gives the iteration number with the total number of expansion vectors given in parenthesis. All remaining entries in the table are given in eV and are relative to the final converged excitation energies. The final converged answers in our implementation agree typically to within 0.0005 eV with the results computed with the RPAC program, due primarily to the use of different physical constants in the two codes. Note that, in order to have a fair comparison of the two methods, in our notation each

TABLE II. Convergence comparison of porphyrin at the 6-31G**/LSDA TDDFT level of theory using two different methods. The calculations are for the three lowest lying singlet excited states on an IBM RS6000/250 workstation. All components of the eigenvectors were converged to four decimal places (Thresh = 10^{-4}).

Method		Total number of		CPU (h)
		Iterations	Vectors	
Davidson	Eq. (16)	36	140	127
non-Hermitian	Eq. (15)	9	68	58

“paired” vector used in the algorithm of Olsen *et al.*¹⁷ is counted as two. Thus both methods start out with an initial set of 24 trial vectors.

The convergence characteristics of any iterative method can be strongly influenced by the initial guess. In the present case, we see that our initial guess is better than that employed in the RPAC program for the low lying roots and not so good for the higher lying roots. In both methods, we observe a monotonic convergence of the different roots. Allowing for the small fluctuations due to the different initial guesses, it is clear that for all practical purposes the convergence characteristics of the two methods seem to be similar.

Furthermore, the computational expense of the two methods is also equivalent, requiring four matrix times vector multiplies for “each” new expansion vector. To be explicit, the algorithm of Olsen *et al.*¹⁷ requires the computation of $\mathbf{A}\mathbf{X}_i$, $\mathbf{A}\mathbf{Y}_i$, $\mathbf{B}\mathbf{X}_i$, and $\mathbf{B}\mathbf{Y}_i$ whereas in our algorithm we need to compute the quantities $(\mathbf{A}+\mathbf{B})|\mathbf{X}+\mathbf{Y}\rangle_i$, $(\mathbf{A}+\mathbf{B})|\mathbf{X}-\mathbf{Y}\rangle_i$, $(\mathbf{A}-\mathbf{B})|\mathbf{X}+\mathbf{Y}\rangle_i$, and $(\mathbf{A}-\mathbf{B})|\mathbf{X}-\mathbf{Y}\rangle_i$. However, for specialized methods that take into consideration the linear combinations of the \mathbf{A} and \mathbf{B} matrices the current algorithm is superior. In particular, when $\mathbf{A}-\mathbf{B}$ is diagonal, the time required for the matrix times vector multiplication is completely negligible. Thus we gain a factor of nearly 2 compared to the algorithm of Olsen *et al.*¹⁷ for the special case of TDDFT, as we shall discuss in the next section.

F. Comparison of the Hermitian and non-Hermitian codes

Given that the $\mathbf{A}-\mathbf{B}$ matrix is diagonal in the nonhybrid TDDFT case, it seems reasonable *a priori*, to implement this special case as given by Eq. (16), which is in the form of a Hermitian eigenvalue problem. This choice is based on the experience with the Davidson algorithm,¹³ which converges rapidly for the usual cases in which it is employed. Of course, it is also possible to solve this problem based on the non-Hermitian algorithm that we have presented above for solving Eq. (15).

In all cases that we have examined, we have observed that the non-Hermitian code requires 30%–40% less expansion vectors than those required by the Davidson algorithm.¹³ One extreme example is represented by freebase porphyrin ($\text{C}_{20}\text{H}_{14}\text{N}_4$). BauernSchmitt and Ahlrichs reported a calculation at the LSDA level of theory that took a total of 21 iterations to converge.¹⁹ We have repeated this calculation, with slightly different basis set, tolerance, and total

TABLE III. Lowest lying singlet states of C_6H_6 at the 6-31+G* level of theory using various theoretical methods.

Symmetry	CIS	RPA	B3LYP	BPW91	LSDA	Experiment
$B_{2u}(\pi \rightarrow \pi^*)$	6.15	5.96	5.40	5.19	5.31	4.9
$B_{1u}(\pi \rightarrow \pi^*)$	6.31	6.01	6.06	5.93	6.10	6.2
$E_{1g}(\pi \rightarrow 3s)$	7.13	7.12	6.34	6.34	6.36	6.33
$A_{2u}(\pi \rightarrow 3p)$	7.45	7.43	6.84	6.87	6.99	6.93
$E_{2u}(\pi \rightarrow 3p)$	7.75	7.74	6.88	6.85	6.98	6.95
$E_{1u}(\pi \rightarrow \pi^*)$	7.94	7.52	6.96	6.84	6.94	7.0

number of roots sought. Our results using both the Hermitian and non-Hermitian schemes are presented in Table II. We confirm BauernSchmitt and Ahlrichs observations that this calculation converges very slowly when the excitation energies are computed using the Hermitian (or Davidson) algorithm. We see that in terms of total CPU time and number of expansion vectors the non-Hermitian code is roughly twice as fast.

III. RESULTS AND DISCUSSION

We present calculated excitation energies obtained for a few molecules that include results using local, gradient corrected and hybrid functionals. All calculations first involved a geometry optimization at the respective level of theory.

As a first example, we present in Table III results obtained for C_6H_6 using a 6-31+G* basis set and compared them to experiment. All calculations were performed at the respective optimized geometries. The CIS results, which are a useful first approximation, give good qualitative agreement with experiment. However, the first excited state, which is known to be a highly correlated state is evidently poorly described by CIS which predicts this state to be 1.2 eV too high. All of the TDDFT results shown in this table constitute a considerable improvement over the CIS and RPA results.

The 6-31+G* basis set of Foresman *et al.*¹⁰ is especially designed for the calculation of anions and is augmented by an additional sp shell to account for Rydberg states. Bauernschmitt and Ahlrichs⁶ performed a number of TDDFT calculations on ethylene and formaldehyde with this basis set and the much larger Sadlej²⁰ basis set. This basis set includes diffuse basis functions of each angular momentum type on each atom: five *s*, three *p* and two *d* functions on the carbon atoms and 3 *s* and two *p* functions on the hydrogen atoms. With exception of the high lying singlet and triplet A_g states of ethylene, where they found a deviation of 0.5 eV, all other results were found to agree within 0.1 eV. Thus the 6-31+G* basis set employed here seems adequate. However, in order to explore the basis set limit for this molecule, we have performed a number of additional calculations which we present in Table IV. The significantly larger basis sets with additional diffuse basis functions indicate that the lowest two states are converged to 0.1 eV, whereas the higher lying excited states are lowered by almost 0.3 eV worsening the agreement with experiment. Nevertheless, comparing the results from Tables III and IV, we see that for states that are well below the ionization threshold the basis set error for a given functional with the 6-31+G* basis is

TABLE IV. Basis set comparison for some of the lowest lying singlet states of C₆H₆. The AUG-prefix is used to add diffuse functions to the cc-pVTZ basis set; it places one *s*, one *p* and one *d* diffuse function on the hydrogen atoms and one *s*, one *p*, one *d* and one *f* function on the carbon atoms.

Symmetry	B3LYP			LSDA		
	6-31+G*	Sadlej	AUG-cc-pVTZ	6-31+G*	Sadlej	AUG-cc-pVTZ
$B_{2u} (\pi \rightarrow \pi^*)$	5.40	5.33	5.34	5.31	5.25	5.26
$B_{1u} (\pi \rightarrow \pi^*)$	6.06	5.99	5.99	6.10	6.02	6.02
$E_{1g} (\pi \rightarrow 3s)$	6.34	6.04	6.01	6.36	6.16	6.19
$A_{2u} (\pi \rightarrow 3p)$	6.84	6.53	6.51	6.99	6.76	6.80
$E_{2u} (\pi \rightarrow 3p)$	6.88	6.56	6.54	6.98	6.75	6.80

smaller than the difference between values obtained using different theoretical methods (e.g., CIS versus B3LYP).

It should be pointed out that the good results obtained here might be significantly worse for higher lying states as pointed out recently and very convincingly by Casida *et al.*⁷ Thus Casida *et al.* show that there is marked deterioration for high lying bound states above the TDLDA ionization threshold (which is at $-\epsilon_{\text{HOMO}}^{\text{LDA}}$); the wrong asymptotic behavior of the LDA exchange-correlation potential leads to a $-\epsilon_{\text{HOMO}}^{\text{LDA}}$ that is much lower than the true ionization potential.

As a second example, we have computed excitation energies for freebase porphyrin and present our results in Table V. There have been a number of calculations done on this molecule including the most recent calculations (equations of motion coupled cluster singles and doubles) of Nooijen and Bartlett.²¹ As pointed out by Bauernschmitt and Ahlrichs,⁶ this molecule has very low lying excited states for which the adiabatic approximation should work best. As is evident from Table V, the TDDFT results rival the very accurate equation of motion coupled cluster singles and doubles (EOM-CCSD) calculations²¹ and are in excellent agreement with experiment. Again, the CIS method predicts vertical excitation energies that are much higher than what is experimentally found.

In a more recent paper by Gwaltney and Bartlett,²² this calculation was repeated with additional polarization functions. We have also repeated a similar calculation using the 6-31G** basis set and present the results in the lower half of Table V. Although the CIS results improve slightly with this larger basis set, the TDDFT results change slightly. The EOM-CCSD results²² with the DZP basis give significantly better agreement with experiment.

Finally, we present results for C₇₀ in Table VI using a 3-21G basis set. We note that the first few lowest lying triplet states are imaginary at the RPA level of theory (i.e., RPA predicts a triplet ground state). In addition, the HF based methods, RPA and CIS, predict vertical singlet excitation energies that are much higher than the TDDFT methods. The TDDFT results seem to be in much better agreement with the available experimental data. The present results could clearly benefit from a much larger basis set. Based on simple quantum defect theory one does not expect Rydberg states to show up at energies that are significantly less than 3 eV below the ionization potential. The present calculations employed the 3-21G basis set to obtain results in a timely manner and should be considered for illustrative purposes only. For C₆₀, for example, the 6-31G+s/RPA method predicted

TABLE V. Excitation energies (in eV) of porphyrin obtained at various levels of theory.

Symmetry	DZ				Experiment (Ref. 23)
	LSDA	B3LYP	CIS	CCSD ^a	
1 $^1B_{1u}$	2.19	2.24	2.48	1.72	1.98
1 $^1B_{2u}$	2.34	2.42	2.60	2.61	2.42
2 $^1B_{1u}$	2.99	3.28	4.46	3.66	3.33
1 $^1B_{3g}$	2.91	3.31	4.67	3.63	
2 $^1B_{2u}$	3.03	3.47	6.12	3.77	3.65
1 1A_g	3.01	3.55	5.56	4.08	
6-31G**					
Symmetry	LSDA	B3LYP	CIS	CCSD ^b	Experiment (Ref. 23)
1 $^1B_{1u}$	2.23	2.28	2.47	1.75	1.98
1 $^1B_{2u}$	2.36	2.44	2.59	2.40	2.42
2 $^1B_{1u}$	3.04	3.33	4.63	3.47	3.33
1 $^1B_{3g}$	2.99	3.42	5.01	3.44	
2 $^1B_{2u}$	3.06	3.51	4.85	3.62	3.65
1 1A_g	3.04	3.61	5.68	3.95	

^aThe EOM-CC results of Nooijen and Bartlett (Ref. 21) employed a DZ basis set on C and N and a STO-3G basis set on H.

^bThis calculation was performed using a DZ basis set with polarization functions (for more details see Ref. 22).

TABLE VI. Excitation energies (eV) of C_{70} as predicted by various methods. All calculations were performed using a 3-21G basis set.

Symmetry	LSDA	B3LYP	RPA	CIS	Experiment (Ref. 24)
$^1A'_2$	1.85	2.20	2.93	3.15	
$^1A'_1$	1.87	2.22		3.99	
$^1E'_1$	1.87	2.22	3.48	3.67	1.9
$^1E'_2$	1.95	2.30	3.56	3.72	
$^1A'_2$	2.00	2.24			
$^1E'_1$		2.44			
$^1E''_1$	2.13	2.53			
$^3A'_2$	1.71	1.57		1.79	
$^3E'_1$	1.74	1.77		2.16	1.4–1.6
$^3E'_2$	1.77	1.97		2.35	
$^3A'_1$	1.79	2.08			
$^3E'_1$	1.83	2.16			
$^3A'_2$	1.85	2.22			
$^3E''_1$	2.04	2.27			
$^3A''_2$	2.07	2.32			
$^3E'_2$	2.12	2.33			
$^3E'_1$	2.13	2.38			

excitation energies¹⁴ that are substantially overestimated and attributed to the limited basis set employed.

IV. CONCLUSIONS

We have implemented an efficient algorithm for the computation of excitation energies using TDDFT within the adiabatic approximation. The results obtained for the few molecules that we and others have studied seem to be quite promising. These studies indicate a significant quantitative improvement at equivalent computational cost over HF based methods such as CIS and RPA.

Preliminary evidence seems to indicate that hybrid functionals yield more accurate excitation energies than gradient corrected functionals,⁶ although an extensive study has not yet been carried out.

We have presented a new algorithm for obtaining the lowest few eigenvectors of large non-Hermitian matrices. This algorithm has similar convergence properties as that presented by Olsen *et al.*,¹⁷ but involves half as many matrix times vector products for the special case of TDDFT that employs nonhybrid functionals. We have also shown evidence that for the pure-DFT case, the algorithm introduced in this paper for the solution of Eq. (15) turns out to be faster than the Hermitian approach of Eq. (16) solved in conjunction with the Davidson algorithm.

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