

Quantum Chemistry of Excited State: Tamm-Dankoff Approximation with Correlated Wave Functions

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A simple derivation of the general equations of the Tamm-Dankoff approximation (TDA) is presented using the equation-of-motion technique to describe electronic excitations in molecules. It is emphasized that the performance of this method strongly depends on the accuracy of the reference (ground) state. Though the Hartree-Fock ground state is commonly applied, the 'all-single CI' (CIS) method based on it is not too reliable. On the other hand, if the ground state is described by sophisticated wave functions like CISD or a coupled cluster ansatz, the TDA equations become quite complicated and may even turn inconsistent. We advocate the use of geminal type ground state wave functions, which, if the strong orthogonality condition is utilized, provide an efficient starting point, being not only highly correlated but also very transparent. Fully consistent TDA equations are derived for strongly orthogonal geminals, which can be of great help in the interpretation of molecular spectra in terms of local contributions and chromophores.

INTRODUCTION

In ground state quantum chemistry, one has the basic guide: the variational principle. Even if some standard methods are not variational in nature (*cf.* the perturbational schemes or the coupled cluster approach), a variational calculation at a similar level of accuracy can always serve as a test of the results.

The theory of excited states, unfortunately, lacks such a clear principle. While the approximate ground state wave function can be always defined as the one minimizing the energy within the given function class, the same does not apply to excited states. From the formal point of view, one may de-

fine the first excited state as the state which minimizes the energy but is orthogonal to the ground state, and so on. However, this definition is not too useful in practice as we usually do not know the exact ground state either. Demanding the excited state wave function to remain orthogonal to an *approximate* ground state is a rather arbitrary auxiliary condition and may cause cumulative inaccuracies in describing excited states.

Therefore, practical treatments of excited states of molecules are usually based on some excitation models, such as the single transition approximation (STA), Tamm-Dankoff approximation (TDA),¹ the random phase approximation (RPA),^{1,2} multi-root configuration interaction (CI) techniques, *etc.* Among these, the TDA is the first level that fulfils the condition of orbital invariance (the requirement that the excited states remain invariant to any unitary transformation within the space of occupied (or virtual) orbitals). This plays, therefore, a fundamental role in the theory of excited states, even if its accuracy is not satisfactory in usual implementations.

In this paper, we shortly review the derivation of the TDA equations using the equation of motion (EOM) technique,² and discuss the conditions by which the standard CIS (CI with single excitations) method³ can be obtained from the general TDA equations. Then, we shall report our recent result, which concerns improvement of the accuracy of the TDA without destroying the mathematical consistency and the simplicity of the formalism.

Numerical calculations will be performed subsequently and reported in a forthcoming paper.

REVIEW OF TDA EQUATIONS

In this Section, we present a short summary of the TDA equations through the equation of motion technique. We use a simplified derivation⁴ which is sufficient for the present purpose; for a more general discussion, see Ref. 1. Consider the Schrödinger equation

$$\hat{H}|n\rangle = E_n |n\rangle. \quad (1)$$

It is convenient to define an *excitation operator* as

$$\hat{O}_n^+ |0\rangle = |n\rangle \quad (2)$$

and the corresponding *de-excitation operator* as

$$\hat{O}_n^- |n\rangle = |0\rangle. \quad (3)$$

In Eqs. (2–3), $|0\rangle$ is the true ground state. We demand that $|0\rangle$ cannot be further de-excited, that is

$$\hat{O}_n^- |0\rangle = |0\rangle . \quad (4)$$

A formal construction of the excitation and de-excitation operators in the bra-ket formalism is clearly:

$$\hat{O}_n^+ = |n\rangle \langle 0| \quad (5)$$

and

$$\hat{O}_n^- = |0\rangle \langle n| . \quad (6)$$

From this latter equation, we see that \hat{O}_n^- is the adjoint of \hat{O}_n^+ .

Let us now study the commutator of the Hamiltonian and the excitation operator. Using Eq. (5), we get:

$$[\hat{H}, \hat{O}_n^+] = \hat{H} |n\rangle \langle 0| - |n\rangle \langle 0| \hat{H} = (E_n - E_0) |n\rangle \langle 0| \quad (7)$$

where the Schrödinger equation (1) was utilized. That is, denoting the excitation energies $(E_n - E_0)$ by ω_n , we have:

$$[\hat{H}, \hat{O}_n^+] = \omega_n \hat{O}_n^+ . \quad (8)$$

By analogy to Heisenberg's equation of motion, this result is usually called the equation of motion (EOM) for the excitation operator.² It is quite interesting that such a simple formal derivation indeed produces something nontrivial: as we shall see below, Eq. (8) can be used in practice to determine the excitation operator \hat{O}_n^+ . It is also obvious from Eq. (2) that the explicit knowledge of \hat{O}_n^+ permits one to construct excited state wave functions. Excitation energies emerge as byproducts when solving Eq. (8).

Solution of Eq. (8) can proceed in the following manner. First, we expand the unknown operators \hat{O}_n^+ as linear combinations of some properly selected fundamental operators \hat{A}_k^+ :

$$\hat{O}_n^+ = \sum_k X_k^n \hat{A}_k^+ . \quad (9)$$

Similarly, the de-excitation operators are expanded in terms of the adjoint fundamental operators

$$\hat{O}_n^- = \sum_k X_k^{n*} \hat{A}_k^- \quad (10)$$

where $\hat{A}_k^- = (\hat{A}_k^+)^\dagger$ and the asterisk denotes complex conjugation of the expansion coefficients X_k^n to be determined from Eq. (8).

Expansions (9–10) do not involve any approximation if the set of fundamental operators is complete in the operator space. In practice, however, one has to use truncated expansions.

Substituting the operator expansions (9) into the EOM (8), multiplying the expanded equations from the left (and from the right) by \hat{A}_L^- , and subtracting the resulting two equations, we get the generalized eigenvalue equations

$$\sum_K \hat{\mathcal{A}}_{LK} X_K^n = \omega_n \sum_K \hat{\mathcal{B}}_{LK} X_K^n \quad (11)$$

where operators $\hat{\mathcal{A}}$ and $\hat{\mathcal{B}}$ are defined by the commutators

$$\hat{\mathcal{A}}_{LK} = [\hat{A}_L^-, [\hat{H}, \hat{A}_K^+]] \quad (12)$$

and

$$\hat{\mathcal{B}}_{LK} = [\hat{A}_L^-, \hat{A}_K^+]. \quad (13)$$

These are the general TDA equations in operator form. Taking the expectation value of Eq. (11) with the ground state, we get the general TDA equations in their matrix form:

$$\sum_K \mathcal{A}_{LK} X_K^n = \omega_n \sum_K \mathcal{B}_{LK} X_K^n \quad (14)$$

where the TDA matrices are defined as

$$\mathcal{A}_{LK} = \langle 0 | [\hat{A}_L^-, [\hat{H}, \hat{A}_K^+]] | 0 \rangle \quad (15)$$

and

$$\mathcal{B}_{LK} = \langle 0 | [\hat{A}_L^-, \hat{A}_K^+] | 0 \rangle. \quad (16)$$

Solution of Eq. (14) consists of two steps: (i) one has to evaluate the TDA matrices according to Eqs. (15,16); and (ii) one has to solve the generalized eigenvalue equations (14).

For evaluation of the matrix elements, we define a set of many-electron wave functions by

$$|K\rangle = \hat{A}_k^+ |0\rangle \quad (17)$$

where $|0\rangle$ is the true ground state satisfying Eq. (1), but the wave functions $|K\rangle$ are *not* eigenfunctions of the Hamiltonian, they merely serve as a basis in the many-electron space. Putting down the adjoint of Eq. (17), we have

$$\langle K | = \langle 0 | \hat{A}_k^- . \quad (18)$$

With the aid of these basis functions, the matrix elements \mathcal{B}_{LK} can be written as

$$\mathcal{B}_{LK} = \langle 0 | \hat{A}_L^- \hat{A}_K^+ | 0 \rangle - \langle 0 | \hat{A}_K^+ \hat{A}_L^- | 0 \rangle = \langle 0 | \hat{A}_L^- \hat{A}_K^+ | 0 \rangle = \langle L | K \rangle . \quad (19)$$

Here, the second term of the commutator vanished due to Eq. (4). That is, provided this consistency requirement is fulfilled, \mathcal{B} is just a metric matrix in the space of many-electron basis functions.

Under the same conditions, the matrix elements \mathcal{A}_{LK} can similarly be transformed to

$$\mathcal{A}_{LK} = \langle L | \hat{H} | K \rangle - E_0 \langle L | K \rangle \quad (20)$$

by which the general TDA equations become

$$\sum_K \langle L | \hat{H} | K \rangle X_K^n = (E_0 + \omega_n) \sum_K \langle L | K \rangle X_K^n . \quad (21)$$

These are analogs to the CI equations, to which they can be reduced in special cases (*vide infra*). To get rid of the ground state energy for Eq. (21) and to simplify further, let us study the matrix elements of the Hamiltonian:

$$\langle L | \hat{H} | K \rangle = \langle 0 | \hat{A}_L^- \hat{H} \hat{A}_K^+ | 0 \rangle = \langle 0 | \hat{A}_L^- (\hat{R}_K^+ + \hat{A}_K^+ \hat{H}) | 0 \rangle = \langle 0 | \hat{A}_L^- \hat{R}_K^+ | 0 \rangle + E_0 \langle L | K \rangle \quad (22)$$

where operators \hat{R}_K^+ are defined as the commutator

$$\hat{R}_K^+ = [\hat{H}, \hat{A}_K^+] . \quad (23)$$

Substituting this into Eq. (21), we finally get the direct-TDA equations

$$\sum_K \langle 0 | \hat{A}_L^- \hat{R}_K^+ | 0 \rangle X_K^n = \omega_n \sum_K \langle L | K \rangle X_K^n . \quad (24)$$

It is to be emphasized that these equations are exact (*i.e.*, they yield the exact excitation energies and excited wave functions) provided the following two conditions are fulfilled:

1. $|0\rangle$ is the true ground state
2. the fundamental operators \hat{A}_k^+ form a complete set.

In this case, the symbol 'A' in acronym 'TDA', referring to 'approximation', is not too fortunate. However, neither of these two conditions can be fully satisfied in practical calculations, and one can merely expect that the better they are fulfilled, the more accurate the solutions of the TDA equations will be.

CIS EQUATIONS

Standard CIS equations are easily recovered from general TDA if the approximations defined by the following two conditions are made:

condition 1. $|0\rangle$ is chosen as the Hartree-Fock ground state:

$$|0\rangle \simeq |HF\rangle = \phi_1^+ \phi_2^+ \dots \phi_n^+ |vac\rangle. \quad (25)$$

condition 2. the fundamental operators A_K^+ are single-particle excitations from the occupied orbital i to the virtual MO p^* :

$$A_K^+ = \phi_{p^*}^+ \phi_i^- \quad (26)$$

where $\phi_{p^*}^+$ and ϕ_i^- are creation and annihilation operators for Hartree-Fock MOs, and label K is now equivalent to the composite index $\{p^* i\}$.

Then, matrix \mathcal{B} is easily evaluated as

$$\mathcal{B}_{LK} = \langle HF | \phi_j^+ \phi_q^- \phi_{p^*}^+ \phi_i^- | HF \rangle = \delta_{pq} \delta_{ij} = \delta_{KL}. \quad (27)$$

Similarly, matrix \mathcal{A} reduces to

$$\mathcal{A}_{LK} = \langle HF | \phi_j^+ \phi_q^- \hat{H} \phi_{p^*}^+ \phi_i^- | HF \rangle - E_{HF} \delta_{ij} \delta_{pq} \quad (28)$$

which can also be evaluated in a straightforward manner. In words, \mathcal{B} is the unit matrix and the first term of \mathcal{A} is the matrix of the Hamiltonian in the space of single excitations with the HF reference state. With these matrices, the TDA equations (14) go over the usual CI equations among singly excited configurations (CIS method).

The CIS approach is known to provide a relatively poor description of excited states.³ In particular, it does not account for correlation effects in a satisfactory manner. However, though the contrary is sometimes stated,³ the CIS excited state does contain some correlation. This can be proven by checking the occupancies of its natural orbitals, which are *fractional numbers* in general, indicating an inherently multiconfigurational behavior.

It is clear from the discussion in the previous Section that all the shortcomings of the CIS method should be traced back to the two approximations listed above. Improvements of this scheme should either involve a better ground state or a more complete description of excitations.

CONSISTENCY REQUIREMENT IN TDA

Besides its simplicity, there is an important advantage of the CIS method: it satisfies the consistency requirement expressed by Eq. (4). This

is an especially appealing feature, which is not trivial to maintain when going beyond the CIS approximation or beyond the TDA scheme. In particular, neither the well-known random phase approximation (RPA),¹ nor TDA-tape schemes with standard correlated reference states will meet this requirement.

To see that Eq. (4) is indeed fulfilled for CIS, we write

$$\hat{O}_n^-|0\rangle = \sum_K X_K^{n*} \hat{A}_K^-|0\rangle = \sum_{ip^*} X_{ip^*}^{n*} \phi_i^+ \phi_{p^*}^- |HF\rangle = 0 \quad (29)$$

where the last equation is true as no virtual can be annihilated from the HF ground state.

If, however, one uses a multideterminantal reference ground state $|\Psi_0\rangle$ instead of $|HF\rangle$, then $\phi_{p^*}^-|\Psi_0\rangle \neq 0$ in general, as $|\Psi_0\rangle$ may have a component in which orbital p^* is occupied. This leads to the consistency requirement being lost, unless special care is taken to define the reference ground state and the excitation space in a consistent manner.

We note that instead of Eq. (4), one could also consider the more general requirement

$$\hat{O}_n^-|m\rangle = \hat{O}_n^- \hat{O}_m^+|0\rangle = \delta_{nm}|0\rangle \quad (30)$$

which expresses the orthogonality of different excited states:

$$\langle n|m\rangle = \langle 0|\hat{O}_n^- \hat{O}_m^+|0\rangle = \delta_{nm}. \quad (31)$$

It is also easy to show that the CIS model fulfils this requirement, as well.

In this paper, we propose to replace condition 1. of the previous Section by using a correlated reference state, and to modify condition, 2. accordingly, in a way allowing the consistency requirement of Eq. (4) to be preserved. The suggested wave function will be described in the next Section.

STRONGLY ORTHOGONAL GEMINALS

Let us define a ground state N -electron wave function with variationally determined strongly orthogonal geminals ψ_i^+ , as their antisymmetrized products (APSG):

$$\Psi_0^{APSG} = \psi_1^+ \psi_2^+ \dots \psi_{N/2}^+ |vac\rangle. \quad (32)$$

The geminals ψ_i^+ -s can be expanded in mutually exclusive orthogonal subspaces to ensure strong orthogonality:

$$\psi_i^+ = \sum_{\mu < \nu}^{(i)} C_{\mu\nu}^i a_\mu^+ a_\nu^+, \quad i = 1, 2, \dots, N \quad (33)$$

where the superscript (i) on the summation indicates that only those indices μ and ν are considered which belong to the subspace assigned to geminal i . In Eq. (32), operators α_μ^+ ($\mu \in i$) create electrons on orbitals spanning the i -th subspace. Although the form of the wave function in Eq. (32) is analogous to the Hartree-Fock case, Eq. (25), Ψ_0^{APSG} is clearly a multi-reference state which consists of many determinants with high excitations.

If the geminals are not fully variational, but the one-particle subspaces are intuitively selected*, we refer to them as strictly localized geminals (SLG).⁵⁻¹³

The algebra of the APSGs is given by

$$[\Psi_i^+, \Psi_k^+] = [\psi_i, \psi_k] = 0 \quad (34)$$

$$[\psi_i, \psi_k^+] = \delta_{i,k} \hat{Q}_i \quad (34)(35)$$

where the quasiparticle commutator has the form^{5,6,10,12,13}

$$\hat{Q}_i = 1 - \sum_{\mu\nu} P_{\mu\nu}^i \alpha_\mu^+ \alpha_\nu \quad (36)$$

with P_i being the first-order density matrix for geminal i , for which, using the convention $C_{\mu\lambda}^i = -C_{\lambda\mu}^i$ for $\mu > \lambda$, we get.^{14,5,12,10}

$$P_{\mu\nu} = \langle \psi_i | \alpha_\mu^+ \alpha_\nu | \psi_i \rangle = \sum_{\lambda}^{(i)} C_{\mu\lambda}^i C_{\nu\lambda}^i \quad (37)$$

Relation (35), which is a consequence of the strong orthogonality of the geminals,¹² is extremely important as it tells us that the quasiparticle creation and annihilation operators *commute* for different geminals. This permits us to use an analogous algebra in the evaluation of matrix elements as if we had a single-reference function. We have to emphasize, however, that this statement applies only to matrix elements in which *no multiple quasiparticle creation operator appear for one subset consecutively*. Extension to a more general case is important when studying excited states; this was done recently and will be published elsewhere.¹⁵

Variational determination of coefficients $C_{\mu\lambda}^i$ is equivalent to solving local Schrödinger equations for each two-electron system in its associated subspace:

$$\hat{H}^i \psi_{ik}^+ |vac\rangle = E_i^k \psi_{ik}^+ |vac\rangle \quad (38)$$

* That is, only the coefficients $C_{\mu\lambda}^i$ are determined variationally for each subspace, not the subspaces themselves.

where \hat{H}^i is the two-electron Hamiltonian for the i -th subspace,⁶ E_i^κ is the energy of the i -th geminal in its κ -th state. The $\psi_i^+ \equiv \psi_{i0}^+$ gives a ground-state geminal used in Eq. (32), while $\kappa > 0$ refers to an excited geminal. For more details of this formalism, we refer to previous publications of our laboratory^{5–8} and to works by other authors.^{16–18, 14,19}

TDA WITH STRONGLY ORTHOGONAL GEMINALS

As mentioned above, the accuracy of TDA is a sensitive function of the exactness of the applied reference state. For a new representation of TDA, which is expected to do a much better job than the CIS method, we introduce the following two approximations:

1. The reference ground state is chosen as Ψ_0^{APSG} of Eq. (32)
2. The fundamental excitation operators are those which replace a ground state geminal to an excited state geminal:

$$\hat{A}_K^+ = \Psi_{p\kappa}^+ \Psi_{i0}^- . \quad (39)$$

That is, K is now the composite label $ip\kappa$. The adjoint operators are clearly

$$\hat{A}_K^- = \Psi_{i0}^+ \Psi_{p\kappa}^- . \quad (40)$$

It is easy to see that this choice does maintain the consistency requirement discussed in Section »Consistency Requirement in TDA«:

$$\hat{O}^- |0\rangle = \sum_K X_K^{n*} \hat{A}_K^- |0\rangle = \sum_{ip\kappa} X_{ip\kappa}^{n*} \Psi_{i0}^+ \Psi_{p\kappa}^- \left| \Psi_0^{\text{APSG}} \right\rangle . \quad (41)$$

The latter equation holds here because $\Psi_{p\kappa}^- \left| \Psi_0^{\text{APSG}} \right\rangle$ is zero due to the proper commutation rules (34–35) and the orthogonality of the geminals for different states k . One can also show that the APSG-TDA model obeys the more general requirement (30) as well.

Evaluation of the TDA matrices \mathcal{A} and \mathcal{B} is straightforward with the APSG-s. However, matrix \mathcal{B} is now not the unit matrix, but the following result applies:

$$\mathcal{B}_{LK} = \left\langle \Psi_0^{\text{APSG}} \left| \Psi_{j_0}^+ \Psi_{q_\lambda}^- \Psi_{p_\kappa}^+ \Psi_{i_0}^- \right| \Psi_0^{\text{APSG}} \right\rangle = \delta_{ij} \delta_{pq} \left(\delta_{iq} \delta_{\lambda\kappa} + (1 - \delta_{iq}) \left\langle \hat{Q}_{ab}^q \right\rangle \right) \quad (42)$$

as the state K is the $i_0 \rightarrow p_\kappa$ excitation while L is $j_0 \rightarrow q_\lambda$.

Evaluation of the TDA matrix \mathcal{A} can also be done, but the result is quite lengthy and it is not reported here. Alternatively, one can use Eq. (24), in which commutators \hat{R}_K in the APSG-TDA approximation are written as

$$\hat{R}_K^+ = [\hat{H}, \hat{A}_k^+] = [\hat{H}, \psi_{p\kappa}^+ \psi_{l0}^-] = \hat{R}_{ip\kappa}^+ \quad (43)$$

by which the direct form of the TDA equations becomes

$$\begin{aligned} \sum_{ip\kappa} \langle \Psi_0^{\text{APSG}} | \psi_j^+ \psi_{q\lambda}^- \hat{R}_{ip\kappa}^+ | \Psi_0^{\text{APSG}} \rangle X_{ip\kappa}^n = \\ = \omega_n \sum_{\kappa} \langle \Psi_0^{\text{APSG}} | \psi_{j0}^+ \psi_{q\lambda}^- \psi_{q\kappa}^+ \psi_{j0}^- | \Psi_0^{\text{APSG}} \rangle X_{jq\kappa}^n. \end{aligned} \quad (44)$$

Evaluation of the matrix element at the l.h.s. can also be done by the geminal commutation rules. Solution of the standard eigenvalue problem Eq. (44) is not difficult computationally, as the dimensionality of the problem is $(N/2)^2 \times M$, where N is the number of electrons in the molecule while M is the number of possible states for a geminal. For a given molecule (given N), only this latter parameter increases with increasing basis sets, thus one should be able to perform accurate large-basis calculations within the proposed scheme.

We note that geminal type wave functions are also useful in connection with the random phase approximation (RPA). For example, Öhrn and Linderberg pointed out that the so-called antisymmetrized geminal power (APG) wave function, where each geminal is identical, serves as an appropriate reference state for RPA calculations.^{20,21}

In summary, we propose a better representation of the general TDA equations by replacing the Hartree-Fock reference state for the APSG ground state, while changing the excitation space simultaneously in a manner that excitation operators destroy a ground state geminal and create another geminal in excited state. Both changes represent a substantial improvement to the standard CIS scheme. The excitation space represented by Eq. (39) describes several types of single and double excitations (in terms of electrons), thus it may be more adequate to describe electronic excitations than the CIS scheme. However, intergeminal charge-transfer type single electron excitations are missing from Eq. (39) – they should be accounted for by a suitable perturbation of the TDA equations. Proper commutation rules followed by strongly orthogonal geminals ensure the inherent consistency of the TDA equations, for we expect better numerical results than the RPA-type schemes that violate the consistency of the formalism. Numerical calculations will be reported in a forthcoming paper.

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SAŽETAK

Kvantna kemija pobuđenih stanja: Uporaba koreliranih valnih funkcija u Tamm-Dankoffovoj aproksimaciji.

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Koristeći se jednadžbama gibanja za elektronsku pobudu u molekulama, na jednostavan su način izvedene opće jednadžbe za Tamm-Dankoffovu aproksimaciju (TDA). Učinkovitost te metode jako ovisi o točnosti referentnog osnovnog stanja. Uobičajena uporaba Hartree-Fockova osnovnog stanja i na njemu zasnovane metode svih jednostrukih konfiguracijskih interakcija (CIS) nije pouzdana. S druge strane, ako se osnovno stanje opiše finijim valnim funkcijama kao što su CISD ili *ansatzom* vezanih grozdova, TDA-jednadžbe postaju zamršene, pa čak i nekonzistentne. U ovom se radu predlaže uporaba geminalnih valnih funkcija kao dobre polazne točke za opis osnovnog stanja. Te funkcije, uz primjenu uvjeta stroge ortogonalnosti ne samo da dobro opisuju korelaciju već su i vrlo transparentne. Izvedene TDA-jednadžbe za strogo korelirane geminale mogu biti korisne u tumačenju ovisnosti molekularnih spektara o lokalnim doprinosima i kromoforima.