Excited States and Electronic Spectroscopy

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March 27, 2008
A Quick Review of the Wavefunction-based ab initio Methods

1. Single reference methods

(Use single determinant SCF wavefunction as a starting point)

Hartree-Fock (HF) or SCF

Configuration interaction (CI), CIS, CISD, etc.

Møller-Plesset (MP) perturbation theory, MP2, MP3, etc.

Coupled-Cluster (CC), CCD, CCSD, CCSDT, etc.

Instead of including all configuration to a particular order as in MP theory, each excited configuration is included to infinite order via an exponential excitation operator:

\[
\Phi_{cc} = e^{\hat{T}} \Phi_0 = \left[ 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \ldots \right] \Phi_0
\]

\[
T_1 \Phi_0 = \sum_{i} \sum_{a} t_{i}^{a} \Phi_{i}^{a}, \quad T_2 \Phi_0 = \sum_{i<j} \sum_{a<b} t_{ij}^{ab} \Phi_{ij}^{ab}
\]

2. Multireference method

(Use a linear combination of CSFs, \( \psi = \sum_{i} C_{i} \Phi_{i} \) and varies not only \( C_{i} \)s but also the coefficients of the orbitals that are used to construct the determinants. CSF stands for “configuration state function”.)

Multiconfigurational SCF (MCSCF)

The most common of these is the Complete Active Space SCF (CASSCF) method. As for any full CI expansion, the CASSCF becomes unmanageably large even for small active spaces.

Multireference configuration interactions, MRCI (Combines the MCSCF and conventional CI)

CASPT2 (implementation of MP2 on CASSCF reference)

CASPT2//CASSF is a very popular, albeit very expensive, method.
Coupled Cluster Methods

\[ \Psi_{cc} = e^{T}\Phi_0 \]  

(1)

\[ e^T = 1 + T + \frac{1}{2} T^2 + \frac{1}{6} T^3 + \ldots = \sum_{k=0}^{\infty} \frac{1}{k!} T^k \]  

(2)

where the cluster operator \( T \) is given by

\[ T = T_1 + T_2 + T_3 + \ldots + T_N \]  

(3)

The \( T_i \) operator acting on a HF reference wavefunction generates all \( i \)th excited Slater determinant, \( \text{viz.} \).

\[ T_1 \Phi_0 = \sum_{i} \sum_{a} t_{i}^{a} \Phi_{i}^{a} \]  

(4)

\[ T_2 \Phi_0 = \sum_{i<j} \sum_{a<b} t_{ij}^{ab} \Phi_{ij}^{ab} \]

Combining eqs. (2) and (3), the exponential operator \( e^T \) may be written as

\[ e^T = 1 + T_1 + \left( T_2 + \frac{1}{2} T_1^2 \right) + \left( T_3 + T_2 T_1 + \frac{1}{6} T_1^3 \right) + \left( T_4 + T_3 T_1 + \frac{1}{2} T_2 T_1^2 + \frac{1}{24} T_1^4 \right) + \ldots \]  

(5)

The first term generates the reference HF and the second all singly excited states. The first parenthesis generates all doubly excited states, the second all triply excited states, and so on.

Using eq. (1), the Schrödinger equation becomes

\[ H e^{T}\Phi_0 = E e^{T}\Phi_0 \]  

(6)

Multiplying from the left by \( \Phi_0^* \) and integrating, we have

\[ \langle \Phi_0 | H e^{T} | \Phi_0 \rangle = E_{cc} \langle \Phi_0 | e^{T} \Phi_0 \rangle \]  

(7)

\[ \langle \Phi_0 | H e^{T} | \Phi_0 \rangle = E_{cc} \langle \Phi_0 | (1 + T_1 + T_2 + \cdots) \Phi_0 \rangle \]

\[ E_{cc} = \langle \Phi_0 | H e^{T} | \Phi_0 \rangle \]

As the Hamiltonian operator contains only one- and two-electron operators, we have
When HF orbitals are used to construct the Slater determinant, the first matrix elements are zero (Brillouin’s theorem), and the second matrix elements are simply two-electron integrals over MOs

\[
E_{cc} = E_0 + \sum_{i<j} \sum_{a<b} \langle \phi_{ij} | \phi_{ab} \rangle \left( t_{ij}^a t_{ij}^b - t_{ij}^a t_{ij}^b \right) \langle \phi_{ij} | \phi_{ab} \rangle
\]

Eq. (10) is exact and contains all possible excited determinants, (as in full CI). For practical reasons, the cluster operator (T) must be truncated at some excitation level.

Inclusion of T_1 only does not give any improvement over HF, as the matrix element between the HF and singly excited states are zero.

1. The lowest level of approximation is therefore, T = T_2. This is referred as Coupled Cluster Doubles (CCD).
2. T = T_1 + T_2 gives Coupled Cluster Singles and Doubles (CCSD).
3. T = T_1 + T_2 + T_3 yields CCSDT.

CCSD is the only generally applicable coupled cluster method. For CCSD,

\[
e^{T_1+T_2} = 1 + T_2 + T_1 + \left( T_2 + T_1 + \frac{1}{2} T_1^2 \right) + \left( T_2 T_1 + \frac{1}{6} T_1^3 \right) + \left( \frac{1}{2} T_2^2 + \frac{1}{2} T_2 T_1 + \frac{1}{2} T_1^2 \right) + \ldots
\]

The CCSD energy and amplitude can be derived by multiplying eq. (6) with a singly excited determinant and integrating

\[
\langle \Phi_m^e | H | (1 + T_1 + \left( T_2 + \frac{1}{2} T_1^2 \right) + \left( T_2 T_1 + \frac{1}{6} T_1^3 \right)) \Phi_0 \rangle = E_{CCSD} \langle \Phi_m^e | T_1^1 \Phi_0 \rangle
\]

\[
\langle \Phi_m^e | H | T_1 \Phi_0 \rangle + \langle \Phi_m^e | H | T_2 \Phi_0 \rangle + \langle \Phi_m^e | H | T_2 T_1 \Phi_0 \rangle + \langle \Phi_m^e | H | T_3 \Phi_0 \rangle = E_{CCSD} \sum_{ia} t_{ia}^e \langle \Phi_m^e | \Phi_i^0 \rangle
\]

\[
\langle \Phi_m^e | H | \Phi_0 \rangle + \sum_{ia} t_{ia}^e \langle \Phi_m^e | \Phi_i^0 \rangle + \sum_{ijab} \left( t_{ij}^{ab} + t_{ij}^{ba} - t_{ij}^{ab} t_{ij}^{ba} \right) \langle \Phi_m^e | H | \Phi_{ijab}^0 \rangle
\]

\[
+ \sum_{ijkabc} \left( t_{ij}^{ab} t_{jk}^{ac} + \ldots + t_{ij}^{ab} t_{jk}^{ac} t_{ik}^{bc} \right) \langle \Phi_m^e | H | \Phi_{ijkl}^0 \rangle = E_{CCSD} t_m^e
\]
Recently developed CC2 (Coupled Cluster approximate double) is derived from CCSD by including only the double contribution arising from the lowest order in perturbation theory (where perturbation is defined as in MP theory). CC3 is an approximation to CCSDT.

Both in terms of computational cost and accuracy,

\[ \text{HF} \ll \text{CC2} < \text{CCSD} < \text{CC3} < \text{CCSDT} \]

**EOM-CC theory**

In the EOM-CC (equation of motion CC) approach to excited states, the excited-state \( x \) wave function is given by simple parameterization of the ground-state \( g \) wave function:

\[ |\psi_x\rangle = R|\psi_g\rangle, \]  

where \( R \) is a linear excitation operator, given by

\[ R = R_0 + R_1 + R_2 + R_3 + \ldots, \]  

\[ R_n = \frac{1}{n!^2} \sum_{ijkl} r_{ij}^{abc} r_{lk}^{ade} \ldots, \]

with \( i, j, k, \ldots \) representing occupied orbitals and \( a, b, c, \ldots \) representing unoccupied orbitals.

The ground-state wave function is given by the CC approximation.

\[ |\psi_g\rangle = e^T|\Phi_0\rangle, \]  

where \( |\psi_g\rangle \) is a single Slater determinant. Substitution of eq. (1) and (4) into the Schrödinger equation yields

\[ H R e^T |\Phi_0\rangle = E R e^T |\Phi_0\rangle. \]  

As \( R \) and \( T \) are excitation operators that commute eq. (5) can be written as

\[ e^{-T} H e^T R |\Phi_0\rangle = E R |\Phi_0\rangle. \]
or
\[ \mathcal{H}\mathcal{R}\Phi_0 = \mathcal{E}\mathcal{R}\Phi_0 \]

where \( \mathcal{H} \) is the similarity transformed Hamiltonian, i.e.,
\[ \mathcal{H} = e^{-T}H e^T. \]

**MMCC (Method of Moments Coupled Cluster)**

Standard CC methods, such as CCSD, CCSD(T), and EOMCC (equation of motion CC), work well for non-degenerate systems and excited states dominated by single excitation from the ground state. For degenerate or quasi-degenerate system and excited states dominated by double excitation from the ground state, biradicals, and other open-shell systems, renormalized coupled-cluster methods have been developed by Piecuch and co-workers. These CC methods, termed as CR-CCSD(T), CR-CCSD(TQ) and CR-EOM-CCSD(T), and size extensive formulations known as CR-CC(2,3), which are all derived from the method of moments of CC equations, are available in the GAMESS package. These are single-reference approaches that eliminate the failure of standard CC methods.

The basic idea of the MMCC theory is that of the non-interative, state-specific, energy corrections
\[ \delta_K^{(A)} = E_K - E_K^{(A)} \]
which, when added to the energies of the ground (\( K=0 \)) and excited (\( K>0 \)) states obtained in the standard CC or EOM-CC calculations (termed method A), recover the exact (full CI) energies \( E_K \). The main purpose of all MMCC calculations is to estimate \( \delta_k^{(A)} \), such that the resulting MMCC energies
\[ E_K^{\text{MMCC}} = E_K^{(A)} + \delta_K^{(A)} \]
are close to the corresponding exact energies \( E_K \).
1. **Ground-State MMCC Theory**

In the single-reference CC theory, the ground-state wave function \(|\Psi_0\rangle\) of an \(N\)-electron system is given by

\[
|\Psi_0\rangle = e^T|\Phi_0\rangle
\]  

(1)

If \(A\) represents the standard single-reference CC approximation, the cluster operator is

\[
T^{(A)} = \sum_{n=1}^{m_A} T_n
\]  

(2)

where \(T_n, n=1, 2, \ldots m_A\) are the many-body component of \(T^{(A)}\).

In all standard CC approximation, the cluster operator \(T^{(A)}\) is obtained by solving the nonlinear algebraic equations

\[
Q^{(A)}H^{(A)}|\Phi_0\rangle = 0
\]  

(3)

where

\[
H^{(A)} = e^{-T^{(A)}}He^{T^{(A)}}
\]  

(4)

and \(Q^{(A)}\) is the sum of projection operators onto the \(n\)-tuply excited configurations relative to reference \(|\Phi\rangle\). By analyzing the relationship between multiple solutions of the nonlinear equations, representing different CC approximations (CCSD, CCSD(T), etc.), Piecuch and Kowalski arrived at an expression for the non-iterative correction \(\delta^{(A)}_0\)

\[
\delta^{(A)}_0 = E_0 - E^{(A)}_0
\]  

(5)

\[
= \sum_{n=m_A+1}^{N} \sum_{k=m_A+1}^{n} \langle \Psi_0 | Q_n C_{n-k}(m_A) M_k(m_A) | \Phi \rangle / \langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle,
\]

where

\[
C_{n-k}(m_A) = (e^{T^{(A)}})_{n-k}
\]

represents the \((n - k)\)-body component of the CC wave operator \(e^{T^{(A)}}\), \(\Psi_0\) is the exact ground-state wave function, and the generalized moments \(M\) is give by
This is the basic equation of MMCC formalism.

2. **Excited-State MMCC**

Recall from the standard EOMCC theory, the excited state $|\psi_K\rangle$ is given by

$$|\psi_K\rangle = R_K|\psi_0\rangle, \quad K > 0$$

The excited-state energies $E_K$ and the corresponding excitation operators $R_K$ are obtained by diagonalizing the similarity-transformed Hamiltonian $\overline{H} = e^{-T}He^T$.

In the exact EOMCC theory, the cluster operator $T$ and the excitation operators $R_K$ are sums of all relevant many-body components that can be written for a given $N$-electron system. In the standard EOMCC approximations, such as EOMCCSD, the many-body expansions of $T$ and $R_K$ are truncated at some excitation level. Thus, if $A$ represents the standard EOMCC approximation, in which the many-body expansions of $T$ and $R_K$ are truncated at the $m_A$-body components with $m_A < N$, we obtain

$$T \simeq T^{(A)} = \sum_{n=1}^{m_A} T_n, \quad (1)$$

$$R_K \simeq R^{(A)}_K = R^{(A)}_{K,0} + R^{(A)}_{K,\text{open}}, \quad (2)$$

Where the ‘open’ part of $R^{(A)}_K$ is defined by

$$R^{(A)}_{K,\text{open}} = \sum_{n=1}^{m_A} R_{K,n}, \quad (3)$$

and $T_n$ and $R_{K,n}$ are the $n$-body components of operators $T^{(A)}$ and $R^{(A)}_K$, respectively. In the EOMCCSD method, $m_A = 2$, in the EOMCCSDT approach, $m_A = 3$, etc. The cluster operator $T^{(A)}$ is obtained by solving eq. (3) of the previous section (section 1), whereas the
excitation operators \( R_k^{(A)} \) are obtained by diagonalizing the similarity-transformed Hamiltonian \( \overline{H}(A) \) in a space spanned by the reference configuration \( |\Phi\rangle \) and the excited configurations included in \( T^{(A)} \) and \( R_k^{(A)} \). The resulting EOMCC equations, defining approximate method A, can be given the following compact form:

\[
(P + Q^{(A)})(\overline{H}^{(A)} - E_k^{(A)} R_k^{(A)} |\Phi\rangle) = 0,
\]

(4)

where \( \overline{H}^{(A)} \) and \( Q^{(A)} \) are defined in the previous sections.

Once the cluster and excitation operators, \( T^{(A)} \) and \( R_k^{(A)} \) are identified, and the ground- and excited-state energies \( E_k^{(A)} (K \geq 0) \) are determined by solving the relevant CC/EOMCC equations, the MMCC corrections \( \delta_k^{(A)} \) can be calculated by using the following expression:

\[
\delta_k^{(A)} = \sum_{n=m_A+1}^{N} \sum_{j=m_A+1}^{n} \langle \Psi^K | Q_n C_{n-j} (m_A) M^{EOMCC}_{K,j} (m_A) |\Phi\rangle / \langle \Psi^K | R_k^{(A)} e^{T^{(A)}} |\Phi\rangle,
\]

(5)

where \( C_{n-j} (m_A) \) is the \((n-j)\)-body component of the CC were operator \( e^{T^{(A)}} \)

\[
C_{n-j} (m_A) = (e^{T^{(A)}})_{n-j}
\]

(6)

and

\[
M^{EOMCC}_{K,j} (m_A) |\Phi\rangle = Q_j (\overline{H}^{(A)} R_k^{(A)} |\Phi\rangle.
\]

(7)

The \( M^{EOMCC}_{K,j} (m_A) |\Phi\rangle \) quantities appearing in eq. (7) can be expressed in terms of the generalized moments of the EOMCC equations defining approximation A, i.e., the left-hand side of the EOMCC eigenvalue problem involving \( \overline{H}^{(A)} \) (the \( (\overline{H}^{(A)} R_k^{(A)}) |\Phi\rangle \) term), projected on the \( j \)-tuply excited configurations relative to \( |\Phi\rangle \):
Density Functional Theory (DFT) methods

1. DFT

DFT is based on the proof by Hohenberg and Kohn (in 1964) that for molecules with a non-degenerate ground state, the energy, wave function, and all other electronic properties of the state is determined by the electron density.

\[ \rho(1) = \int |\psi(1,2 \ldots N)|^2 d\omega_1 d\tau_2 \ldots d\tau_n \]  

Although Hohenberg-Kohn theorem confirms the existence of a functional relating the electron density and the energy of a system, it does not tell us the form of such functional. In 1965, Kohn and Sham developed, with the introduction of atomic orbitals, a formulation that yields a practical way to solve the Hohenberg-Kohn theorem for a set of interacting electrons.

In analogy to wave function methods, the functional that connects the energy \( E \) to \( \rho \), \( E[\rho] \), can be separated into an kinetic energy contribution, \( T[\rho] \), nuclear-electron attraction, \( V_{ne} \), and the electron-electron repulsion, \( V_{ee}[\rho] \):

\[ E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \]  

The last term can be decomposed into Coulomb and exchange terms, \( J[\rho] \) and \( K[\rho] \). With this separation, the energy functional can be written as

\[ E_{DFT}[\rho] = T_S[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \]  

where the subscript \( S \) denotes that it is the kinetic energy calculated from a Slater determinant and \( E_{xc} \) is the so-called exchange correlation function. \( T_S \) can be calculated by
\[ \mathbf{T}_s = \sum_{i=1}^{n} \left\langle \phi_i \left| -\frac{1}{2} \nabla^2 \right| \phi_i \right\rangle \]  

(4)

where \( \phi_i \) is the Kohn-Sham orbitals that satisfies the Kohn-Sham equation

\[ h_{KS} \phi_i = \varepsilon_i \phi_i \]  

(5)

where

\[ h_{KS} = -\frac{1}{2} \nabla^2 + V_{\text{eff}}, \quad V_{\text{eff}} = V_{\text{ne}}(r) + \int \frac{\rho(r')}{|r-r'|} dr' + V_{\text{xc}}(r). \]  

(6)

where \( V_{\text{XC}} \) is the functional derivative of the exchange-correlation energy, given by

\[ V_{\text{XC}}[\rho] = \frac{d E_{\text{XC}}[\rho]}{d \rho}. \]  

(7)

The electron density \( \rho \) is related to the KS orbital by

\[ \rho(r) = \sum_{i=1}^{n} |\phi_i(r)|^2 \]  

(8)

The importance of the KS orbitals is that they allow density to be calculated. The solution of the KS equation proceeds in a self-consistent fashion, starting from a crude charge density, which could be simply the superposition of the atomic densities of the constituent atoms. An approximate form for the functional that describes the dependence of the \( E_{\text{XC}} \) on the electron density is then used to calculate \( V_{\text{XC}} \). This allows the KS equation to be solved, yielding initial set of KS orbitals. This set of orbitals is then used to calculate a improved density from eq. (8). This procedure is repeated until the density and the exchange-correlation energy satisfies a convergence criterion.

The exact form of Exchange correlation functional, \( E_{\text{xc}}(\rho) \) is currently unknown. Approximate \( E_{\text{xc}}[\rho] \) are however available in various forms. Most existing exchanges correlation functionals are split into a pure exchange and correlation contribution, i.e.,

\[ E_{\text{xc}}[\rho] = E_x[\rho] + E_c[\rho] \]  

(9)
One of the simplest DFT methods is the local density approximation (LDA), which assumes that the density behaves like a uniform (or homogeneous) electron gas. LDA constitutes the simplest approach to represent the exchange-correlation \((xc)\) functional, by assuming that the exchange energy at any point in space is given by that of a uniform electron gas,

\[
E_x^{\text{LDA}}[\rho] = -C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}
\]

\[
e_x^{\text{LDA}}[\rho] = -C_x \rho^{1/3},
\]

where \(\epsilon\) represents the energy per particle (energy density).

Molecular systems are, however, very different from a homogeneous electron gas in that their density \(\rho(\mathbf{r})\) is especially inhomogeneous. Generalized gradient approximation (GGA) methods take into account by making the exchange and correlation energies dependent not only on the density but also on the gradient of the density \(\Delta \rho(\mathbf{r})\). In the LDA, the paired electrons with opposite spin have (or occupy) the same KS orbital. The local spin density approximation (LSDA), on the other hand, allow the electrons (with opposite spins) to have different KS orbitals, in analogy with UHF method. Generally LDA and LSDA do not lead to an accurate description of molecular properties, but GGA leads to much more satisfactory results.

Currently the most popular GGA, also called gradient-corrected functional, are those derived by Lee, Yang and Parr (LYP) or those obtained by Perdew (P86), which are combined with successful gradient-corrected exchange functional of Becke88 to yield exchange correlation functionals, known as the acronyms BLYP and BP86.

A great advantage of the DFT method over the wave function-based methods is in its computational costs or economy. This arises from the fact that whereas the wave function for an \(n\)-electron molecule is functional of \(3n\) spatial coordinates and \(n\) spin coordinates, the density is a function of only the three spatial coordinates. For this reason, DFT is applicable to fairly large molecular systems. The computational effort is similar to a SCF calculation, but since DFT
implicitly includes some amount of electron correlation, the accuracy of DFT is often similar to that obtained with MP2, or even better. The weakness of DFT at present is the inability to systematically improve upon $E_{xc}[\rho]$ and have it coverage towards the exact Born-Oppenheimer energy (like one might conceivably do in a wave function-based CI or CC calculations with correlation consistent basis sets.)

2. *Time-Dependent Density Functional Theory (TDDFT)*

TDDFT is an alternative formulation of time-dependent quantum mechanics that extends the basic ideas of the ground-state DFT to the treatment of time-dependent phenomena, especially electronic excitation. It has its foundation in the Gross and Runge, who formulated a time-dependent version of the Kohn-Sham scheme.

In the time-dependent perturbation theory of quantum mechanics, the linear response is measured by the change in the expectation value $\langle q \rangle$ of one-electron operator represented by $q$ when a time-dependent electric field $E_\omega \cos \omega t$ is applied, i.e.,

$$ q = q^0 + \sigma(\omega) E_\omega \cos \omega t $$

The perturbation theory gives the following expression for the tensor $\sigma$:

$$ \sigma(\omega) = \sum_k \left[ \frac{\langle 0|q|k\rangle\langle k|q|0\rangle}{\omega_k^2 - \omega^2} \right] $$

If the operator $q$ is the dipole operator ($q = e \cdot r$), then $\sigma$ is polarizability and the excitation energies would be obtained as the poles of the frequency dependent polarizability.

The Fourier transforms of the first order change in the density $\delta \rho(r, \omega)$ and of a scalar time-dependent change in the external potential $\delta \nu_{ext}(r, \omega)$ can be related by the full linear response function $\chi(r, r', \omega)$:

$$ \delta \rho(r, \omega) = \int \text{d}r' \chi(r, r', \omega) \delta \nu_{ext}(r', \omega) \quad (1) $$
However, it is very difficult to find good approximations for this linear response function, since it requires in principle the knowledge of all exact eigenfunctions and excitation energies of the system. The time-dependent DFT alternative is to use the response function $\chi_s(r,r',\omega)$ of the non-interacting Kohn-Sham system, in combination with an effective or screened potential $\delta u_{\text{eff}}(r,\omega)$:

$$\delta \rho(r,\omega) = \int dr' \chi_s(r,r',\omega) \delta u_{\text{eff}}(r',\omega).$$

This response function requires the knowledge of the occupied and virtual Kohn-Sham orbitals $\{\phi\}$ and energies $\{\varepsilon\}$, as well as the occupation number $n$, which are all obtained in a standard DFT calculation:

$$
\chi_s(r,r',\omega) = \sum_{\text{occ.}} \sum_{\text{virt.}} n_i \phi_i(r) \phi_m(r) \phi_m(r') \phi_i(r') \\
\times \left( \frac{1}{(\varepsilon_i - \varepsilon_m) + \omega} + \frac{1}{(\varepsilon_i - \varepsilon_m) - \omega} \right).
$$

The change in the effective potential $\delta u_{\text{eff}}(r,\omega)$, which depends upon the density change $\delta \rho(r,\omega)$ is given by:

$$
\delta u_{\text{eff}}(r,\omega) = \delta u_{\text{ext}}(r,\omega) + \int dr' \frac{\delta \rho(r',\omega)}{|r-r'|} + \delta u_{\text{xc}}(r,\omega).
$$

The change in the exchange correlation potential is given in terms of the Fourier transform of the so-called exchange correlation kernel $f_{\text{xc}}(r,r';\omega)$

$$
\delta u_{\text{xc}}(r,\omega) = \int dr' f_{\text{xc}}(r,r';\omega) \delta \rho(r',\omega).
$$

The set of equations (2), (3), (4) and (5) must be solved self-consistently. After this has been done, the frequency-dependent polarizability $\alpha(\omega)$ is directly available, for a density change $\delta \rho_i(r,\omega)$ due to an external potential $\delta u_{\text{ext}}(r,t) = E_r \cos(\omega t)$:

$$
\alpha_{ij}(\omega) = -\frac{2}{E} \int dr \delta \rho_i(r,\omega) r_j,
$$
TDDFT has emerged as an alternative to the conventional HF-based single excitation theories such as CI with single substitutions (CIS). The computational costs and complexity of TDDFT are roughly comparable to those of CIS, but the accuracy of TDDFT is superior to that of CIS. Thus, TDDFT is applicable to fairly large systems for which accurate but computationally more demanding excited-state theory (such as CASSCF, CASPT2 and MRCI) are not feasible.

An important factor that determines the accuracy of TDDFT excitation energies is the exchange correlation functional used in the calculation. The TDDFT calculations using non-hybrid exchange correlation tend to underestimate excitation energies of states that have significant charge transfer character, due to spurious self-interaction. Errors are particularly large for local exchange correlation functionals, viz. LDA and LSDA. Examples of hybrid GGA functionals that include a portion of exact HF exchange are B3LPY, B3P86, and B3PW91. Of these, the most popular is B3LYP.

\[ E_{xc} = E_{x}^{GGA} + C_{x}E_{x}^{exact} + E_{c}^{GGA} \]

The use of these hybrid functionals yields good accounts of the vertical excitation energies of the excited states with substantial charge transfer character. For excited electronic states of relatively small dipole moments, the TDDFT vertical excitation energies are in very good agreement (<0.2 eV) with experimental values for a number of molecular systems that have been investigated.

Just as HF methods, increasing size of basis set allows better and better description of the KS orbitals and excitation energies.
Summary of Electronic Structure Methods

A. Wavefunction Based Methods

1. Single reference methods

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<th>Ground State</th>
<th>Excited State</th>
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<tr>
<td>HF (SCF)</td>
<td>CIS (also called Tamn Dancoff Approxn.)</td>
</tr>
<tr>
<td>CC (singles, doubles and triples)</td>
<td>CC2,(^a) EOMCCSD(^b)</td>
</tr>
<tr>
<td>MP (especially MP2)</td>
<td>CIS(D): a second order pertubation expansion, analogous to MP2</td>
</tr>
<tr>
<td></td>
<td>CIS-MP2 (not size consistent)</td>
</tr>
</tbody>
</table>

\(^a\) CC2 is derived from CCSD by including only the doubles contribution arising from lowest (non-zero) order in perturbation theory.

\(^b\) More recently, new versions of CC theory have been developed for treating excited states. One of these, equation-of-motion EOM-CCSD, has given very good results for vertical excitation energies. Analytical gradients for the EOM-CCSD method are available allowing calculation of geometry and vibrational frequencies of excited states.

2. Multireference methods

<table>
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<th>Ground State</th>
<th>Excited State</th>
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<tr>
<td>CASSCF</td>
<td>CASSCF</td>
</tr>
<tr>
<td>CASPT2</td>
<td>CASPT2 (CASPT2//CASSCF, in particular)</td>
</tr>
<tr>
<td>MRCI</td>
<td>MRCI</td>
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3. Single reference wavefunction based method for multireference applications

<table>
<thead>
<tr>
<th>Ground State</th>
<th>Excited State</th>
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<tbody>
<tr>
<td>CR-CCSD(T)</td>
<td>CR-EOMCCSD(T)</td>
</tr>
</tbody>
</table>

B. Density Based Methods

<table>
<thead>
<tr>
<th>Ground State</th>
<th>Excited State</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>TDDFT</td>
</tr>
</tbody>
</table>

Quantum Chemistry Programs:

TDDFT is available in the Gaussian and TURBOMOLE.

The renormalized CC methods, such as CR-CCSD(T) and CR-EOMCCSD(T), are available in the GAMESS package.

CIS(D) is the TURBOMOLE; CIS-MP2 is in the Gaussian, but needs to be tweaked to get it going.
AB INITIO QUANTUM CHEMISTRY PROGRAMS  (Quantum Chemistry, Levine (15.15))

This section surveys some of the available ab initio quantum chemistry program packages.

The program Gaussian (www.gaussian.com/), which exists in various versions ( . . . Gaussian 92, Gaussian 94, Gaussian 98, . . . ) labeled by release year, is a widely used versatile program package that includes all common ab initio methods, such as Hartree–Fock, CI, MCSCF, density-functional, MP (Section 15.18), CC (Section 15.19) and also includes many semiempirical methods. Gaussian 98 includes the molecular-mechanics method. Gaussian can optimize geometries, calculate vibrational frequencies, thermodynamic properties, and NMR shielding constants, search for transition states, calculate MEPs, and include the effects of a solvent. Gaussian is available in versions for supercomputers, workstations, and PCs running Windows. A literature survey found that in 1993 Gaussian was by far the most widely used quantum chemistry program package (D. Boyd in K. Lipkowitz and D. Boyd, Reviews in Computational Chemistry, Vol 6, Wiley, Chapter 5).

GAMESS (General Atomic and Molecular Electronic Structure System) is an ab initio program with fewer calculation methods than Gaussian but with the advantage of being free. It runs on supercomputers, workstations, Power Macintoshes, and Windows PCs and in 1993 was the second-most widely used ab initio program in the above survey. For details, see www.msg.ameslab.gov/GAMESS/GAMESS.html or M. W. Schmidt et al., J. Comput. Chem., 14, 1347 (1993).

Q-Chem (www.q-chem.com/), first released in 1997, is an ab initio package that allows calculations on large molecules (several hundred atoms) and can do Hartree–Fock, MP2, and density-functional calculations. It incorporates methods such as CFMM and ONX to achieve linear scaling (Section 15.5) for large molecules.

Jaguar (www.psgvb.com/) is a fast program that uses the pseudospectral method (Section 15.5) and can do HF, MP2, density functional, and GVB (Section 15.25) calculations [R. A. Friesner, et al., J. Phys. Chem. A, 103, 1913 (1999)].

The ACES II program (www.qtp.ufl.edu/Aces2/) is designed for performing CC and MP (Sections 15.19 and 15.18) calculations.

TurboMole (tchibm8.chemie.uni-karlsruhe.de/PC/TheoChem/) is a program that fully uses molecular symmetry and runs on workstations and Intel PCs using the LINUX operating system.

Molpro (www.tc.bham.ac.uk/molpro/) is an ab initio program designed for highly accurate calculations on small molecules and includes many electron-correlation methods including MCSCF and MR-CI.

CADPAC (Cambridge analytical derivatives package, ket.ch.cam.ac.uk/) is an ab initio program that contains Hartree–Fock, density-functional, and commonly used correlation methods.

The following programs have very good graphical interfaces.

SPARTAN (www.wavefun.com/) includes ab initio (Hartree–Fock and MP2), density functional, semiempirical, and molecular mechanics methods, has several conformational searching methods and runs on workstations. MacSPARTAN, MacSPARTAN Plus, PC SPARTAN, PC SPARTAN Plus, and PC SPARTAN Pro are
smaller versions (Hartree–Fock, semiempirical, molecular mechanics, and for PC SPARTAN Pro, MP2 and density-functional methods) that run on PCs.

HyperChem (www.hyper.com/) includes Hartree–Fock, semiempirical, and molecular mechanics methods and runs on Windows PCs and workstations.

A study using a test set of low-level to very high-level ab initio Gaussian 94 calculations on small molecules [M. C. Nicklaus et al., J. Chem. Inf. Comput. Sci., 38, 893 (1998)] found that a Pentium II 400 MHz PC using the Linux operating system performed about as fast as some of the workstations and was faster than supercomputers. The paradoxically poor performance of supercomputers was partly because many users share a supercomputer.
Renormalized CC methods (CR-SCCSD(T), CR-CCSDT(Q), and CR-EOMTCCSD(T)


Time Dependent DFT (TDDFT)


CC and DFT


Simulation of Electronic Spectra

The intensity of a vibronic transition is proportional to the square of the transition moment, $M_{ev}$, which is given by

$$M = \int \psi_{ev}^* \mu_e \psi_{ev} d\tau_{ev}$$

where $\mu$ is the electric dipole moment operator and $\psi_{ev}$ and $\psi_{cv}$ represent the vibronic wave functions of the final and initial states, respectively. Adopting the Born-Oppenheimer approximation

$$\psi_{ev} = \psi_e \psi_v$$

we have

$$M = \int \psi_{c}^* \mu_e \psi_c d\tau_c \int \psi_{v}^* \psi_v d\tau_v$$

The square of the vibrational overlap integral is known as the Franck-Condon (FC) factor, \textit{viz.}

$$\text{FC factor} = \left| \int \psi_{v}^* \mu_e \psi_v d\tau_v \right|^2.$$  

The simulation of electronic absorption or emission spectra requires the calculation of a number of vibrational overlap integrals. These are usually computed under the harmonic approximation, by using recursion formulas and displacement parameters $B_i$ (for totally symmetric modes) defined by

$$B_i = \left( \frac{\omega_i}{\hbar} \right)^{1/2} Q_{i(R)}^{P,R}$$

Here $Q_{i(R)}^{P,R}$ is the projection of the geometry change between the two states P and R, expressed in Cartesian coordinates, on the R-state normal coordinate $Q_i^R$, i.e.,

$$Q_{i(R)}^{P,R} = [x_p - x_r] M^{1/2} L_i^R$$
where $X_K$ is the $3N$ dimensional vector of the equilibrium Cartesian coordinates in the $K$-th state, $M$ is the $3N \times 3N$ diagonal matrix of the atomic masses, and $L_i^R$ is the $3N$ vector describing the normal coordinate $Q_i^R$, in terms of mass-weighed Cartesian coordinates.

The Franck-Condon (FC) structure of the absorption/emission spectra is calculated by projecting the difference of optimized geometries of the two electronic states involved in the transition onto the normal coordinates of the final state. The displacement parameters for totally symmetric modes are then used to calculate FC factors for individual vibronic transitions. These individual transitions are usually broadened with a Gaussian line-shape of a given half-width to produce the calculated vibronic structure of the electronic transition.
Comparison of CR-EOM-CCSD(T) vertical excitation energies (eV) of adenine with the results CASPT2//CASSCF calculations

<table>
<thead>
<tr>
<th>State</th>
<th>CASPT2 $^a$</th>
<th>CASPT2 $^b$</th>
<th>CASPT2 $^c$</th>
<th>CR-EOM-CCSD(T) $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi\pi^*$</td>
<td>4.74</td>
<td>4.96</td>
<td>5.01</td>
<td>4.90</td>
</tr>
<tr>
<td>$n\pi^*$</td>
<td>5.00</td>
<td>5.16</td>
<td>5.05</td>
<td>4.94</td>
</tr>
</tbody>
</table>


$^d$ Present work.
Comparison of TDDFT adiabatic excitation energies of 4-DMABN with CASPT2 calculations and experiment. Computed dipole moments of the $\pi\sigma^*$ and TICT states are given in parenthesis.

<table>
<thead>
<tr>
<th>State</th>
<th>Experiment $^a$</th>
<th>CASPT2 (10, 9)$^b$</th>
<th>CASPT2 (12, 12)$^c$</th>
<th>B3LYP $^d$</th>
<th>B-P $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1\text{B}_2 (\text{LE, } L_b)$</td>
<td>4.02 $^e$</td>
<td>4.05</td>
<td>3.99</td>
<td>4.28</td>
<td>3.91</td>
</tr>
<tr>
<td>$2^1\text{A}_1 (L_a)$</td>
<td>&lt; 4.56 $^f$</td>
<td>4.41</td>
<td>4.39</td>
<td>4.50</td>
<td>4.13</td>
</tr>
<tr>
<td>$1^1\text{A}_2 (\pi\sigma^*)$</td>
<td>&lt; 4.09 $^g$</td>
<td>4.50 (15.5 D) $^h$</td>
<td>4.20 (14.9 D)</td>
<td>3.47 (16.7 D)</td>
<td></td>
</tr>
<tr>
<td>TICT</td>
<td>3.94 $^f$ (15.6 D)</td>
<td>3.72 (15.0 D) $^h$</td>
<td>3.46 (15.4 D)</td>
<td>2.59 (15.9 D)</td>
<td></td>
</tr>
</tbody>
</table>

$a$ Gas phase.

$b$ Ref. 34 (for wagging angle of $0^\circ$).

$c$ Ref. 35.

$d$ Present work.

$e$ 0–0 transition energy in a supersonic free jet (Ref. 16).

$f$ Vertical transition energy from electron energy loss spectra (Ref. 36).

$g$ Onset of fluorescence break-off in supersonic free jet (Ref. 16).

$h$ Ref. 10.
<table>
<thead>
<tr>
<th>Method</th>
<th>Scaling behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>$N^3$</td>
</tr>
<tr>
<td>HF</td>
<td>$N^4$</td>
</tr>
<tr>
<td>MP2</td>
<td>$N^5$</td>
</tr>
<tr>
<td>MP3, CISD, CCSD</td>
<td>$N^6$</td>
</tr>
<tr>
<td>MP4, CCSD(T)</td>
<td>$N^7$</td>
</tr>
<tr>
<td>MP5, CCSDT</td>
<td>$N^8$</td>
</tr>
</tbody>
</table>