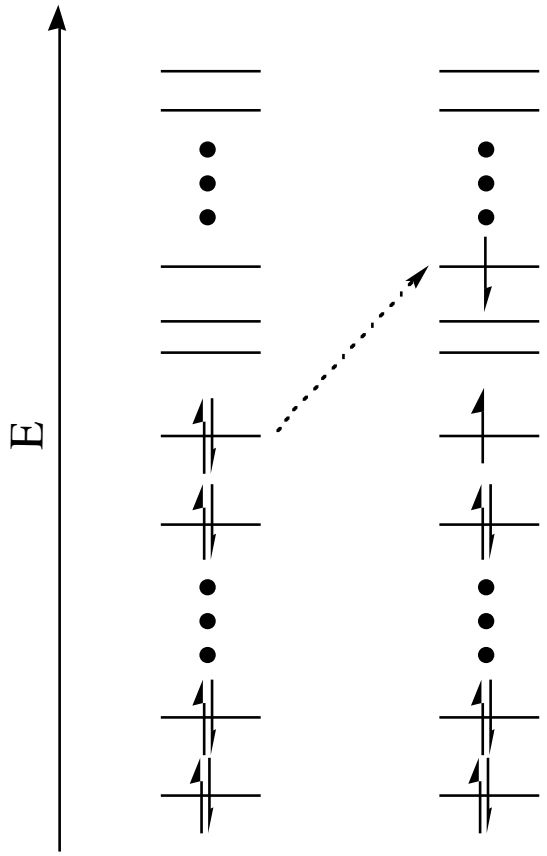
Excited Electronic States

Determinantal/configurational representation of excited states

An excited electronic state is one in which at least one electron is not in as low energy orbital as it could be given the molecular geometry. Such a state may be generated by various processes: absorption of radiation by the ground state or as the product of a chemical reaction. Although unstable relative to collapse to the lower energy ground state, some excited states may have significant lifetimes owing to inefficient coupling with the ground state.

Given *M* doubly occupied molecular orbitals and *N* empty virtual orbitals (and possibly some number of singly occupied orbitals), the number of possible excited states that can be generated is very large. The usual way the chemists think about an excited state is to take the ground state Ψ_0 as reference.



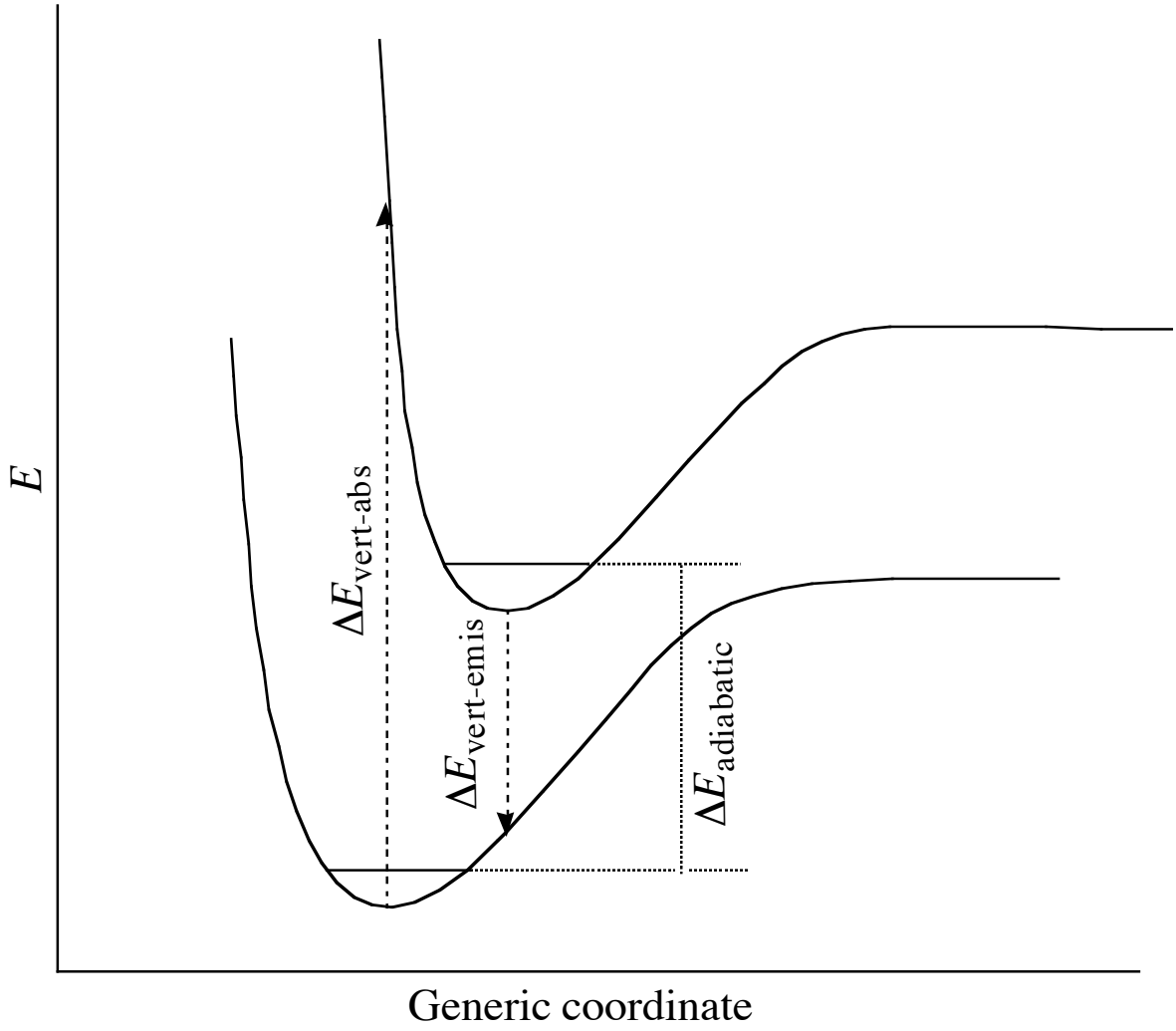
One considers an excited state to be generated by the removal of one electron from the HOMO of the ground state and its placement into some higher-energy orbital. Since the wave function for the ground state can be represented as a single Slater determinant, $^1\Psi_0 = \left|\psi_1^2\psi_2^2\psi_3^2\cdots\psi_{N/2}^2\right\rangle$, then the excited state might in general be written as

$$\Psi_{N/2}^a = \left|\psi_1^2\psi_2^2\psi_3^2\cdots\psi_{N/2}\overline{\psi}_a\right\rangle$$

If an orbital is not doubly occupied, it is multiplied by an α spin unless there is a bar over it, in which case it is multiplied by a β spin function.

An excited state may have singlet or triplet multiplicity: $^1\Psi_{N/2}^a$ or $^3\Psi_{N/2}^a$.

A time scale separation that usually is valid is the Born-Oppenheimer separation of the nuclear and electronic motions.



When the optimal geometry of the ground state is not the same as that for the excited state, we may view the absorption of radiation as taking place at the ground-state geometry, and the energy involved is called the 'vertical' excitation energy. On the timescale of nuclear dynamics, the geometry of the excited state ultimately relaxes to its own optimum. The energy difference ΔE (corrected by ZPE) between the two systems taking each to be at its own optimal geometry is referred to as 'adiabatic' excitation energy. The same can be applied to the reverse process, emission.

The excitation and emission energies are often expressed not in energy units but instead in terms of the wavelength of radiation corresponding to that energy:

$$\Delta E = \frac{hc}{\lambda}$$

h – Planck's constant; c – the speed of light in a vacuum, λ - the radiation wavelength. A larger ΔE value is equivalent to a shorter wavelength, so one says that vertical excitations are blue-shifted (since blue light is on the short wavelength side of the visible spectrum) relative to adiabatic excitation energy, while vertical emissions with smaller ΔE values are red-shifted (red being at the opposite end of the visible spectrum) relative to the same adiabatic energy. The difference between the vertical excitation and emission energies (or wavelengths) is referred to as the Stokes shift.

In terms of computing adiabatic energy differences, if the Born-Oppenheimer PES for the excited state can be computed, geometry optimization of that state may be carried out using the standard techniques. But how then to obtain an excited state wave function and energy?

The simplest approach is to maintain the minimum-determinantal description and reoptimize all the orbitals. However, such an approach is only practical only in cases where the ground-state and excited-state wave functions differ by symmetry – belong to different irreducible representations of the molecular point group. Otherwise, the variational solution for the excited-state wave function will simply collapse back to the ground-state wave function. In certain favorable instances, one can force the SCF equations to converge to different determinants of the same electronic state symmetry, but this happens rare.

Singly excited states

For an average molecule, there are typically one or more low-energy excited states that may reasonably well described as valence-MO-to-valence-MO electronic excitations. Certain states are referred to as $n \rightarrow \pi^*$, $\pi \rightarrow \pi$, etc., indicating the orbital from which the electron is excited on the left into which it is excited on the right.

SCF applicability

Ideally, one would like to study excited states and ground states using wave functions of equivalent quality. Ground-state wave functions can very often be expressed in terms of a single Slater determinant formed from variationally optimized MOs, with possible accounting for electron correlation effects taken thereafter. Such orbitals are determined in the SCF procedure.

However, the problem of variational collapse typically prevents an equivalent SCF description for excited states. Any attempt to optimize the occupied MOs with respect to the energy will necessarily return the wave function to that of the ground state. Variational collapse can sometimes be avoided, when the nature of the ground and excited states prevents their mixing within the SCF formalism. This situation occurs most commonly in symmetric molecules, where electronic states belonging to different irreducible representations do not mix in the SCF, and also in any situation where the ground and excited states have different spin.

CI singles

For many singly excited states, ΔSCF calculations are not an option under any circumstances. The simplest way to calculate excited state energies is configuration interaction with single excitations (CIS). The CIS waver function is $\Psi_k = \sum_{i}^{occupied} \sum_{a}^{virtual} c_{aik} \Psi_i^a$.

The coefficients *c* are the components of the eigenvector for state *k*. The coefficients are optimized by solving the CI secular equation,

$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22}-E & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN}-E \end{vmatrix} = 0$$

and wave function Ψ_k corresponds to the *k*th root of this equation. This process does not involve any orbital reoptimization, and it provides a wave function that is roughly equivalent in quality only to an HF wave function for the ground state. Thus, CIS is not a very accurate method. Example: for excited states of benzene, the CIS results are qualitatively useful, insofar as the states are correctly ordered, and the error is fairly systematic – all states are predicted to be too high in energy by an average of 0.7 eV.

To improve CIS results beyond their roughly HF quality, various options may be considered. For spectroscopic predictions, semiempirical parametrization of the CIS matrix elements may replace their direct computation. The most complete realization of this approach – INDO/S parametrization by Zerner and coworkers. Improvement of ab initio CIS may be achieved by inclusion of the effect of double excitations on the CIS state energy: CIS(D) method by Head-Gordon and coworkers (1994).

Rydberg states

A particular type of singly excited states: Rydberg states – the excited electron has an energy very near the level of the continuum, i.e., it is almost detached. Such states may be conveniently be thought of as an electron attached to a molecular cation that acts as a central attractor, much as a nucleus acts as a central attractor in an atom. Thus, formal Rydberg orbitals may be of s, p, d, etc. character.

The Rydberg orbitals are by nature extremely diffuse compared to valence orbitals. As a result, any attempt to describe a Rydberg state requires either a very complete AO basis set or additional basis functions specifically tailored to Rydberg character that are not necessarily atom-centered (could be centered at the molecular center). At a minimum, basis sets incorporating diffuse orbitals on heavy atoms should be used.

General excited state methods

Electronic states that cannot be well described as single excitations from the ground state require more general formalisms. Of course, these more general formalisms considered below, can be as well applied to singly excited states, but they tend to be more demanding in terms of computational resources, making methods like CIS economical alternatives when they can be applied.

Higher roots in MCSCF and CI calculations

In the process of determining the expansion coefficients in an MCSCF wave function,

$$\Psi = a_0 \Psi_{HF} + \sum_{i}^{occ.} \sum_{r}^{vir.} a_i^r \Psi_i^r + \sum_{i<j}^{occ.} \sum_{r<s}^{vir.} a_{ij}^{rs} \Psi_{ij}^{rs} + \ldots \quad ,$$

CI calculations are carried out in the space of the orbitals that are active in the MCSCF. Excited states that can be generated by electronic excitations within that active space then have a corresponding root in that limited CI window, and one can variationally optimize the orbitals for a root other than the one of lowest energy. In some cases, the root in question is dominated by a single CSF (a single determinant), allowing one to describe the state conveniently by reference to the ground state. In other instances, that will not be the case, and simple relationship between the excited state and the ground state cannot be easily formulated.

In any case, once a root is specified, the MCSCF process minimizes the energy for that root following the usual variational procedure. To correct for dynamical electron correlation, the usual multi-reference methods may be applied, such as CASPT2 and MRCI.

Propagator methods and time-dependent DFT

If a molecule is subjected to a linear electric field **E** fluctuating as

$$\mathbf{E} = \mathbf{r}\cos(\omega t)$$

Where **r** is the position vector in one dimension, t is time, and ω is the frequency of fluctuation, it can be shown that the frequency-dependent polarizability is well approximated by

$$\langle \alpha \rangle_{\omega} = \sum_{i \neq 0}^{states} \frac{\left| \langle \Psi_0 | r | \Psi_i \rangle \right|}{\omega - \left(E_i - E_0 \right)}$$

The numerator of each term in the sum is a so-called transition dipole moment, denominator involves the frequency and the energies of the excited states and the ground state. If the frequency corresponds exactly to the difference in energy between an excited state and the ground state, there is a pole in the frequency-dependent polarizability, i.e., it diverges since the denominator goes to zero. Using propagator methodology (sometimes also called a Green's function approach or an equation-of-motion (EOM) method), the poles of the frequency-dependent polarizability can be determined without having to compute all of the necessary excited-state wave functions and their corresponding state energies. The necessary matrix equations are quite complex. Within the so-called random-phase approximation (RPA) the integrals that are required to compute the excitation energies are essentially those required to fill the CI matrix containing all single and double excitations and the transition dipole moments between the ground state and all singly excited configurations.

Because the RPA method includes double excitations, it is usually more accurate than CIS for predicting excited state energies. However, the method does not provide a formal wave function, as CIS does. The RPA method may be applied to either HF or MCSCF wave functions.

A DFT method that is strongly analogous to RPA is called time-dependent DFT (TDDFT). In this case, the KS orbital energies and various exchange integrals are used instead of matrix elements of the Hamiltonian. TDDFT is usually most successful for low-energy excitations. Casida et al. (1998) have suggested that TDDFT results are most reliable if (i) the excitation energies should be significantly smaller than the molecular IP and (ii) promotions should not take place into orbitals with positive KS eigenvalues.

Energies (eV) for singlet excited states of benzene

Excited state	CIS	RPA	TD-BPW91	TD-B3LYP	Expt.
$^1B_{2u}$	6.15	5.96	5.19	5.40	4.9
$^1B_{1u}$	6.31	6.01	5.93	6.06	6.29
$^1E_{1g}$	7.13	7.12	6.34	6.34	6.33
$^1A_{2u}$	7.45	7.43	6.87	6.84	6.93
$^1E_{2u}$	7.75	7.74	6.85	6.88	6.95
$^1E_{1u}$	7.94	7.52	6.84	6.96	7.0
Mean abs. err.	0.7	0.6	0.1	0.1	

Bauerschmidt and Ahlrichs (1996) considered a large number of excitation energies in ethylene, formaldehyde, N_2, and pyridine. With BP86 and B3LYP functionals (and large basis sets), they found mean absolute errors of ~7 kcal/mol in excitation energies for transitions at energies lower than 1/2 IP. RPA and CIS MAEs for these excitations were 20 and 38 kcal/mol, respectively. More recently, Fabian (2001) compared B3LYP TDDFT results to INDO/S various absorptions in 76 organosulfur compounds.

In general, the performance of the TDDFT approach was quite good; the MAEs over all absorption maxima was 0.21 eV, as compared to 0.35 eV for INDO/S.

Meanwhile, with currently available functionals, TDDFT results are not reliable for Rydberg states and, in general, for electronic transitions in which an electron is transferred to a remote region in space (for example, charge transfer states).

Transition Probabilities

In electronic spectroscopy, one wants to know not only the energy difference between distinct electronic states but also the probability that a transition between them will take place under appropriate circumstances. Thus, in recording of a classic UV/Vis spectrum for a molecule, the wavelength of absorption indicates the energetics of the transition, while the intensities of the absorptions indicate their 'allowedness', or probability.

The absorption intensity is related to the transition dipole moment between the initial and final states:

$$\mu_{fi} = \int \Psi_f \mu \Psi_i d\tau \qquad\qquad \boldsymbol{\mu} = e\mathbf{r}$$

r is the electric field vector. Transition dipole moment is a measure of the dipole moment associated with the shift of charge that occurs when the electron redistribution takes place. The oscillator strength is related to this moment by $f = \frac{8\pi^2 m_e \nu}{3he^2} \times \left|\mu_{fi}\right|^2$

Oscillator strength determined in experiment, $f = \left(\frac{4 m_e c \varepsilon_0}{N_A e^2} \ln 10\right) \times A$ is related to the integrated absorption coefficient *A*, the sum of absorption coefficients over the entire band, $A = \int \varepsilon(\nu) d\nu$. Thus, theoretical and experimental oscillator strengths may be compared.