Introduction to Excited Electronic States

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Excited Electronic State

- Ultraviolet / visible (UV/vis) spectra are dominated by electronic transitions
- Electronic transitions typically occur in the 1-12 eV range (10,000-100,000 cm^{-1})
- 10,000-50,000 cm^{-1}: electronic transitions involving rearrangement of valence electrons; transitions on the lower-energy end of this range often involve unsaturated compounds (molecules with double bonds)
- 50,000-100,000 cm^{-1}: Valence and Rydberg transitions; a Rydberg transition is a promotion of an electron from a valence orbital into a very large/diffuse orbital, so that the final state looks like a cation plus a loosely associated electron
- 100,000 cm^{-1}: High-energy transitions that often lead to ejection of an electron (ionizing or autoionizing states)

Example UV/Vis Spectrum

- Spectrum is broadened by solvent or pressure
- Computed spectrum will be a “stick spectrum” unless artificially broadened or additional steps taken
- Can compute intensities

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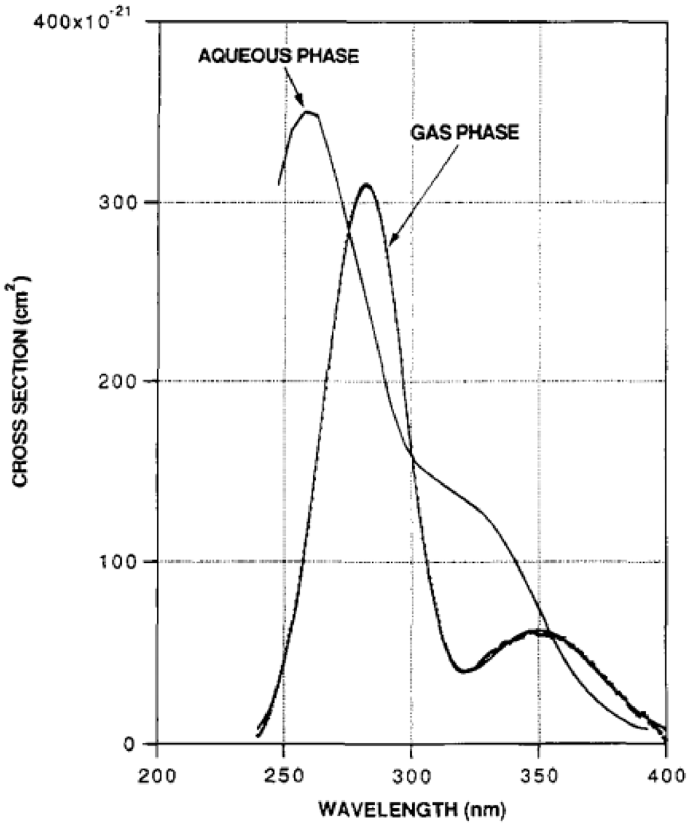


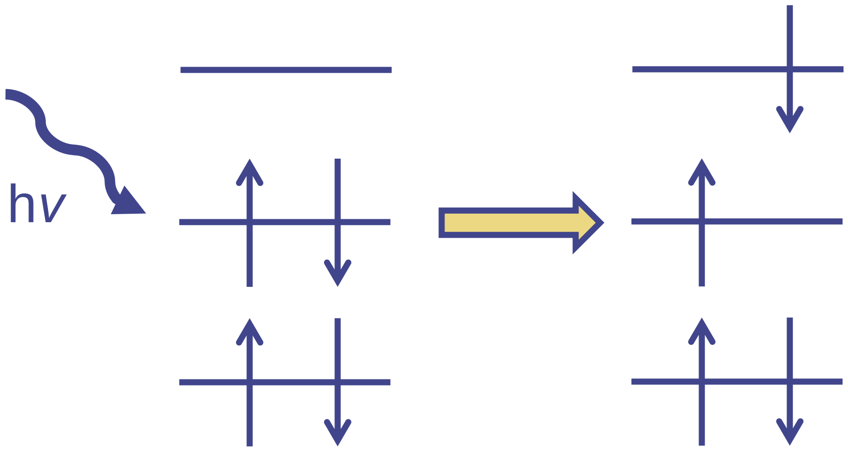
Figure 5. UV/visible absorption spectrum of HOBr obtained in this work. Small squares, measured data. Solid line, parametrized fit to the measured data. Also shown for comparison is the aqueous phase spectrum of HOBr from ref 19.

Transition Intensities

The intensity of a transition between electronic states *p* and *q* is proportional to the “oscillator strength”

$$f_{pq} = \frac{2}{3}\frac{m_e}{\hbar^2}\left(E_q - E_p\right) \underbrace{\sum_{\alpha=x,y,z} \left|\langle \Psi_p | \hat{\mu}_\alpha | \Psi_q \rangle\right|^2}_{\text{Transition dipole moment}}$$

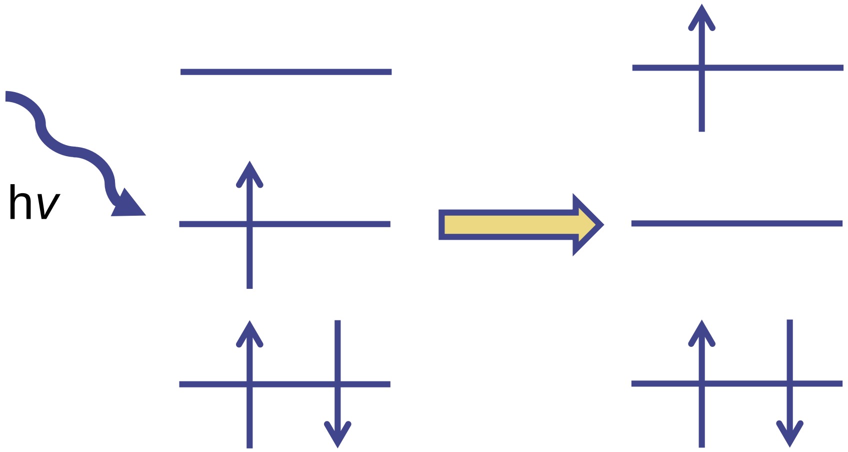
Modeling Excited States



Problem: HF and DFT programs used for ground states don't usually know how to handle open-shell singlets

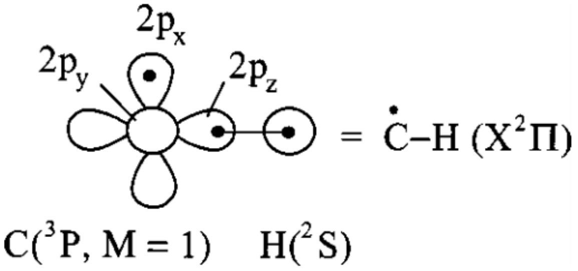
(Could also reach excited state triplets via spin-orbit coupling, etc.)

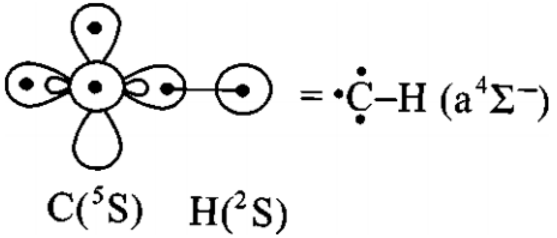
Modeling Excited States

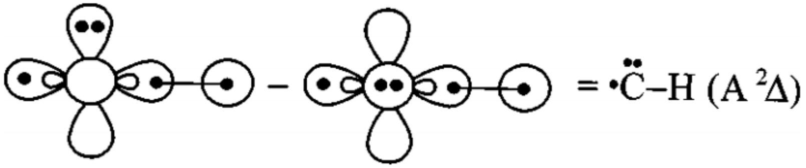


Problem: Ground state methods will find the *lowest* state of a given symmetry. But the excited state may be the 2nd, 3rd, etc., state of that symmetry

Lewis Structure Pictures of Excited States







$$|a\,^4\Sigma^-\rangle = 0.99|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1 1\pi_y^1\rangle$$

$$|A\,^2\Delta\rangle \approx 0.69\{|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2\rangle - |1\sigma^2 2\sigma^2 3\sigma^1 1\pi_y^2\rangle\}$$

$$\begin{aligned}|c\,^4\Sigma^-\rangle = &-0.55|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1 1\pi_y^1\rangle\\ &+0.51|1\sigma^2 2\sigma^1 3\sigma^2 1\pi_x^1 1\pi_y^1\rangle\\ &-0.40|1\sigma^2 2\bar{\sigma}^1 3\sigma^1 4\sigma^1 1\pi_x^1 1\pi_y^1\rangle\\ &-0.26|1\sigma^2 2\sigma^2 4\sigma^1 1\pi_x^1 1\pi_y^1\rangle,\end{aligned}$$

A. Kalemos, A. Mavridis, A. Metropoulos, *J. Chem. Phys.* **111**, 9536 (1999)

Excited State Potentials

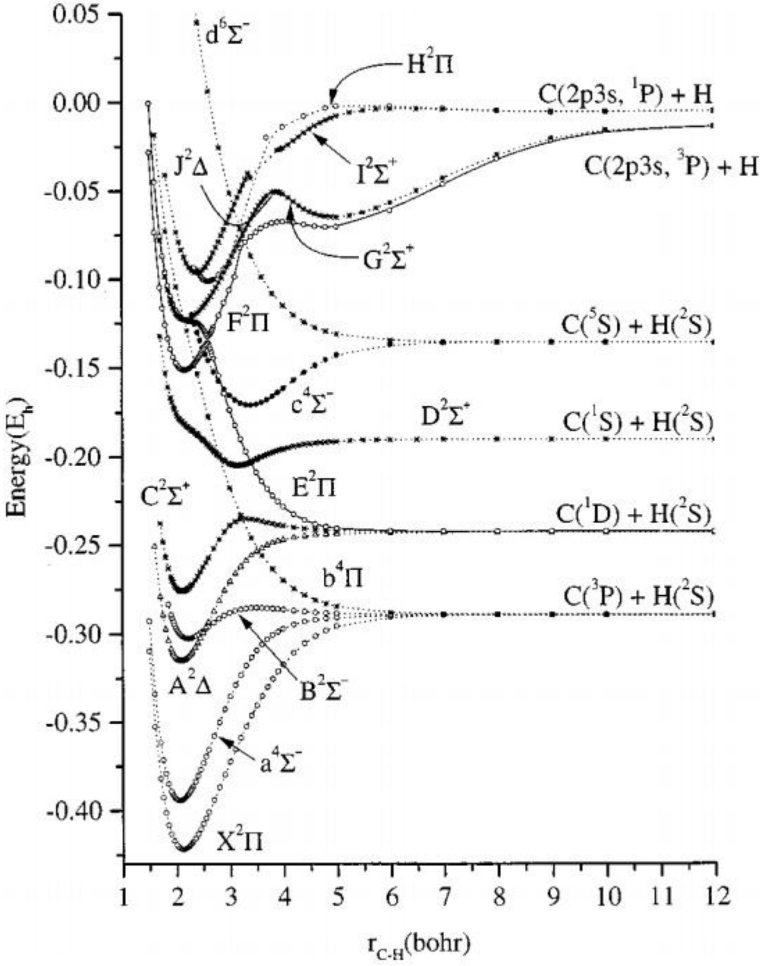


FIG. 1. Potential energy curves of the lowest 11 valence and 4 Rydberg states of CH. All energies have been shifted by +38.00 hartree.

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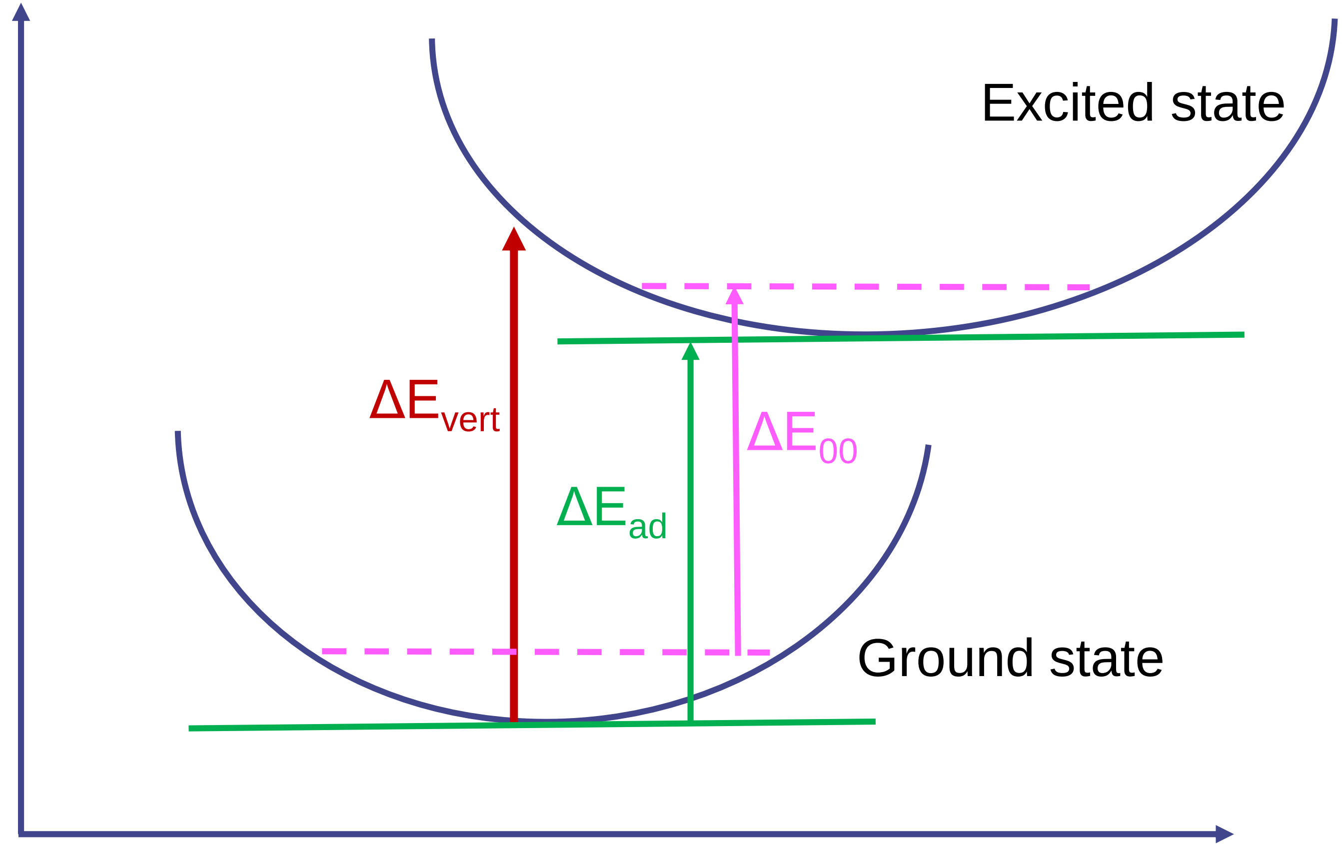
Vertical vs Adiabatic Excitation Energies



Types of Excited States

- Valence states: electrons move from one valence orbital to another (e.g., $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$) (lower-energy states)
- Rydberg states: electrons move into a very large, diffuse orbital (molecule M looks like a cation plus a loosely associated electron) (higher-energy)
- Core-excited states: core electrons are promoted into valence or Rydberg orbitals (very high energy)

Valence vs Rydberg States

- Experimentally, valence states often appear as broad features in the spectrum, whereas Rydberg states are often sharp transitions
- Rydberg transitions often occur in a series that can be fit to the formula

$$h\nu = \epsilon_i - \frac{R}{(n-\delta)^2}$$

where h is Planck's constant, ν is the frequency of the absorbed/emitted light, ε_i is the ith ionization potential of the molecule, R is the Rydberg constant, n is the “quantum number” and δ is the “quantum defect” (a correction factor that is 0-1)

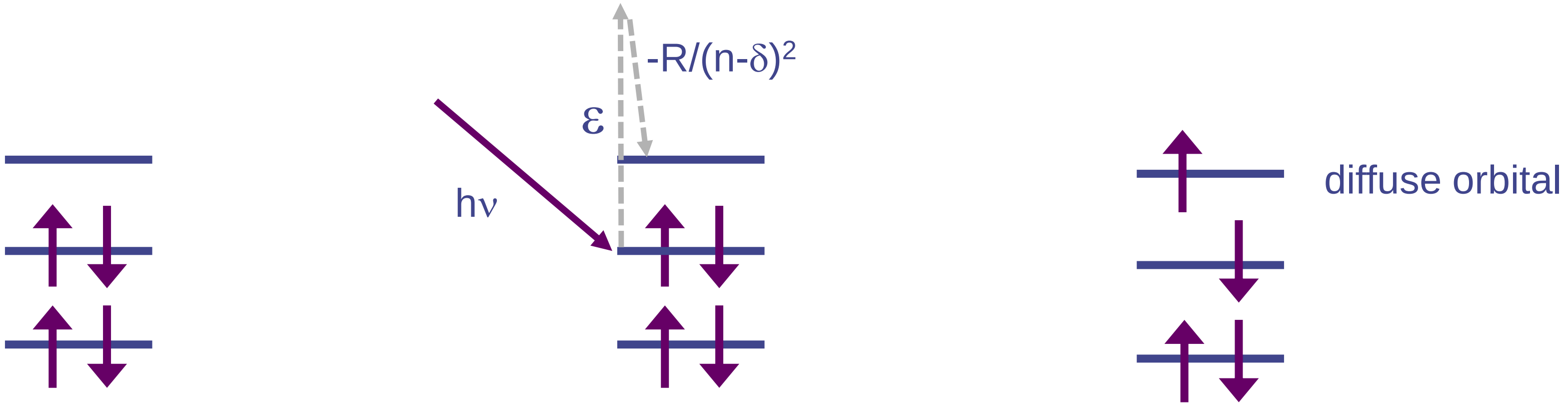
Understanding the Rydberg Energies

$$h\nu = \epsilon_i - \frac{R}{(n-\delta)^2}$$

energy of incoming photon

Energy needed to rip off an e^-

energy of an electron in H atom with principal quantum number n, with correction factor δ



1. Initial state of molecule

2. Light promotes electron

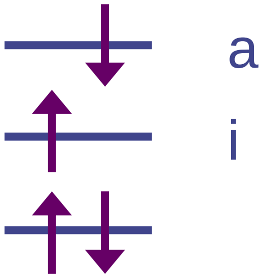
3. “Ionized” molecule + diffuse electron

Multi-determinantal Nature of Excited States

- This excited state should have a 50:50 contribution from both determinants shown --- they should have equal energies
- This is an open-shell singlet
- Our excited state method needs to be able to handle multi-determinant excited states
- This does *not* imply that we have to use multi-reference methods… some “single-reference” methods can be generalized to handle multi-determinantal *excited states*

Single-Determinant Descriptions of Excited States

$$|\Phi_i^a\rangle =$$



- Recall that when we discussed electron correlation, we introduced "excited" or "substituted" determinants that promote one or more electrons from orbitals that are occupied in the Hartree-Fock determinant to orbitals that are unoccupied in the Hartree-Fock determinant
- These excited determinants very roughly describe excited electronic states
- However, these determinants are not very good descriptions of excited states because (a) the orbitals are optimal for the ground state, not the excited state, and (b) excited states tend to be multi-determinantal in nature (see previous slide)
- So, we need a multi-determinant expansion for excited states, not single determinants

Excited States

Excited electronic states represent higher-energy solutions of the electronic Schrödinger equation

$$\hat{H}_{el}(\mathbf{r};\mathbf{R})\Psi^{i}(\mathbf{r};\mathbf{R}) = E^{i}_{el}(\mathbf{R})\Psi^{i}(\mathbf{r};\mathbf{R})$$

Two ways to get them:

- Solve the electronic Schrödinger equation for multiple roots!
- Use response theory

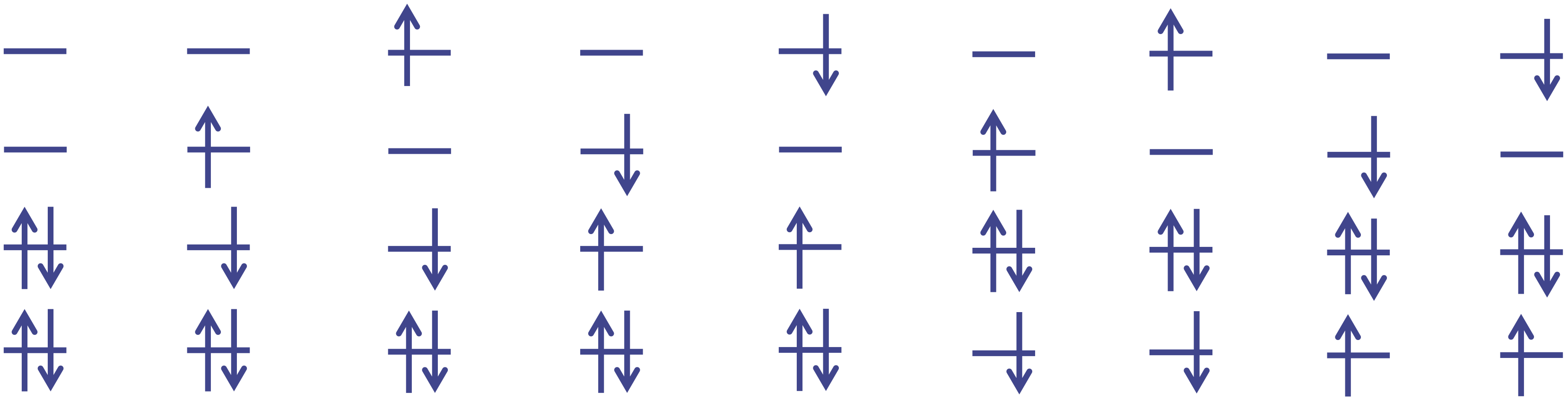
Response Theory Formulation

If the molecule is subjected to an oscillating electric field $E = E_0\, r \cos(\omega t)$, then the frequency-dependent polarizability of the molecule is approximately

$$\langle\alpha\rangle_\omega = \sum_{i\neq 0}^{\text{states}} \frac{|\langle\Psi_0|\mu|\Psi_i\rangle|^2}{\omega - (E_i - E_0)}$$

We can identify excitation energies, $\Delta E = (E_i - E_0)$, from the poles of $<\alpha>_\omega$, where $\omega = \Delta E$

Configuration Interaction Singles (CIS)



- Simplest *ab initio* treatment of excited states
- Has necessary determinants to describe open-shell singlets
- Without any double excitations, this treatment lacks dynamical electron correlation (like "Hartree-Fock quality" for excited states)

Configuration Interaction Singles Hamiltonian Matrix

$$\begin{array}{c|c|c|}
 & |\Phi_0\rangle & \text{singles } |\Phi_j^b\rangle \\ \hline
\langle\Phi_0| & E_0 & 0 \\ \hline
\text{singles } \langle\Phi_i^a| & 0 & \langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle \\ \hline
\end{array}$$

- Fairly inaccurate for excitation energies (errors ~1eV)
- Can correct ground and excited state energies with second-order perturbation theory using CIS(D) of Head-Gordon (errors ~0.5eV)

CISD for Excited States

- CISD would include double excitations from the g.s. (providing dynamical correlation)
- But singly-excited states would need triple excitations (with respect to the g.s.) to get dynamical correlation
- Hence, CISD treats the g.s. better than the e.s.'s, leading to substantially overestimated excitation energies
- CISD is not recommended for excited state studies

Time-Dependent Density Functional Theory (TDDFT)

- Use linear response theory on top of DFT to find the excitation energies
- This leads to the Casida equations, which can be a little complicated to solve
- We can simplify the Casida equations using the "Tamm-Dancoff" approximation (TDA), which yields results that are just as good

Accuracy of TDDFT

- For valence excited states, errors ~0.3eV
- For Rydberg or charge-transfer states, regular TDDFT is not appropriate because electrons feel the wrong long-range potential (should go as ~-1/R)
- Hartree-Fock exchange gives the correct potential; can use 100% Hartree-Fock exchange at long range via "Range Separated Hybrid" functionals (e.g., ωB97X-D, ωPBE)
- Alternatively, can use "asymptotically corrected" functionals (e.g., CAM-B3LYP

Equation-of-Motion Coupled-Cluster (EOM-CCSD)

- Excited state version of CCSD; treats excited states at similar quality as the ground state
- Solve the usual CCSD equations to get the single and double excitation amplitues T_1 and T_2
- Then perform a similarity transformation of the Hamiltonian using these amplitudes
- Then essentially perform a CISD with this transformed Hamiltonian, generating singly and doubly excited states out of the CCSD g.s.
- Works very well for singly-excited states (errors ~0.2 eV) and ok for doubly-excited states

EOM-CCSD Equations

$$|\Psi\rangle = \hat{R}e^{\hat{T}}|\Phi_0\rangle$$

$$\begin{aligned}\hat{R}|\Phi_0\rangle &= \left(\hat{R}_0 + \hat{R}_1 + \hat{R}_2\right)|\Phi_0\rangle \\ &= r_0|\Phi_0\rangle + \sum_{ia} r_i^a|\Phi_i^a\rangle + \sum_{i<j,a<b} r_{ij}^{ab}|\Phi_{ij}^{ab}\rangle\end{aligned}$$

$$\overline{H}\hat{R}|\Phi_0\rangle = E\hat{R}|\Phi_0\rangle$$

$$\overline{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$$

Other PT and CC type approaches

- There is no MP2 for excited states (closest analogue is CIS(D))
- It is difficult or impossible to formulate a (T) correction that works as well for EOM-CCSD as it does for g.s. CCSD; hence, there is no EOM-CCSD(T)
- CC2 is intermediate in quality between MP2 and CCSD; there is EOM-CC2
- CC3 is not quite as good as CCSD(T) but there is EOM-CC3

Multiconfiguration Self-Consistent Field (MCSCF)

- Can get excited states just as higher roots of the CI in the MCSCF
- With a well-chosen active space, can treat g.s. and e.s. at comparable quality, yielding reasonable excitation energies
- Good accuracy will require some kind of post-MCSCF treatment of dynamical correlation, e.g., CASPT2 or multi-reference CI (MRCI)
- This approach, unlike the others mentioned in this talk, will work even if bonds are formed/broken, or for partially filled d/f subshells

Semi-empirical Methods

- There are some semi-empirical methods adapted for excited-state computations, like ZINDO (named after Mike Zerner)
- These have been largely supplanted by TD-DFT, but they remain an interesting option for very large molecules

Excited State Geometry Optimization

- Need this to get adiabatic excitation energies
- Analytic gradients are available for CIS, CIS(D), TDDFT, CASSCF, CASPT2, and even EOM-CCSD
- Can run into problems if excited state surfaces cross each other; this makes it hard to stay on the excited state you want