Electronic Structure Theory
TSTC Session 1

1. **Born-Oppenheimer approx.- energy surfaces**
2. Mean-field (Hartree-Fock) theory- orbitals
3. Pros and cons of HF- RHF, UHF
4. Beyond HF- why?
5. First, one usually does HF-how?
6. Basis sets and notations
7. MPn, MCSCF, CI, CC, DFT
8. Gradients and Hessians
9. Special topics: accuracy, metastable states

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The Schrödinger equation for N electrons and M nuclei of a molecule:

$$\mathbf{H(r,R)}\ \Psi(\mathbf{r,R},t) = \mathbf{i}\hbar\ \partial\Psi(\mathbf{r,R},t)/\partial t,$$

or, if H is t-independent, ($\Psi(\mathbf{r,R},t) = \Psi(\mathbf{r,R})\ \mathbf{exp(-iEt/}\hbar\mathbf{)}$)

$$\mathbf{H(r,R)}\ \Psi(\mathbf{r,R}) = E\ \Psi(\mathbf{r,R})$$

$|\Psi(\mathbf{r,R})|^2$ gives probability density for finding electrons at

$\mathbf{r} = \mathbf{r}_1\mathbf{r}_2\ \mathbf{r}_3\ \ldots\ \mathbf{r}_N$ and nuclei at $\mathbf{R}_1\ \mathbf{R}_2\ \mathbf{R}_3\ \ldots\mathbf{R}_M$.

H contains electronic kinetic energy: $T_e = -\hbar^2/2 \Sigma_{j=1,N} m_e^{-1} \nabla_j^2$

Nuclear kinetic energy: $T_M = -\hbar^2/2 \Sigma_{j=1,M} m_j^{-1} \nabla_j^2$

electron-nuclei Coulomb potentials: – $V_{eM} = -\Sigma_{j=1,M} Z_j \Sigma_{k=1,N} e^2/|r_k - R_j|$

Note the signs!

nuclear-nuclear Coulomb repulsions: + $V_{MM} = \Sigma_{j<k=1,M} Z_j Z_k e^2/|R_k - R_j|$

and electron-electron Coulomb repulsions: + $V_{ee} = \Sigma_{j<k=1,N} e^2/r_{j,k}$

It can contain more terms if, for example, external electric (e.g., $\Sigma_{k=1,N}$ e$\mathbf{r}_k \bullet \mathbf{E}$) or magnetic fields $-(e\hbar/2m_e)\beta_e \Sigma_{k=1,N} \mathbf{S}_k \bullet \mathbf{B}$ are present

What is the reference zero of Hamiltonian energy?

In the **Born-Oppenheimer (BO)** approximation/separation, we (first) *ignore the T_M motions of the nuclei* (pretend the nuclei are fixed at specified locations **R**) *and solve*

$$H^0 \psi_K(\mathbf{r}|\mathbf{R}) = E_K(\mathbf{R}) \psi_K(\mathbf{r}|\mathbf{R})$$

*the so-called **electronic Schrödinger equation**.*

$\mathbf{H^0}$ contains all of H except $\mathbf{T_M}$ (*T_e plus all of the potential energy terms)*.

This is why we say we "freeze the nuclei" in making the BO approximation.

We don't really freeze them; we just solve first for the motions of the electrons at some specified (i.e., frozen set of nuclear positions) **R** values, and we account for the motions of the nuclei later. Why? Electrons move fast compared to nuclei.

Because H^0 is a Hermitian operator in **r**-space, its eigenfunctions form a complete and orthonormal set of functions of **r**

$< \psi_L(\mathbf{r}|\mathbf{R})|\psi_K(\mathbf{r}|\mathbf{R})> = \delta_{L,K}$ (note- the integration is only over $d\mathbf{r}_1 d\mathbf{r}_r \ldots d\mathbf{r}_N$)

$\Sigma_K\, |\psi_K(\mathbf{r}|\mathbf{R})>< \psi_K(\mathbf{r}\}\mathbf{R})| = \mathbf{1}$ (for any values of **R**)

So, the **r**-dependence of Ψ can be expanded in the $\{\psi_K\}$:

$$\Psi(\mathbf{r},\mathbf{R}) = \Sigma_K\, \psi_K(\mathbf{r}|\mathbf{R})\, \chi_K(\mathbf{R}).$$

The $\psi_K(\mathbf{r}|\mathbf{R})$ depend on **R** because H^0 does through

$$-\Sigma_{j=1,M} Z_j \Sigma_{k=1,N}\, e^2/|\mathbf{r_k}-\mathbf{R_j}| + \Sigma_{j<k=1,M}\, Z_j Z_k e^2/|\mathbf{R_k}-\mathbf{R_j}|$$

The $\chi_K(\mathbf{R})$ also depend on **R.**

This expansion ($\Psi(\mathbf{r},\mathbf{R}) = \Sigma_K \psi_K(\mathbf{r}|\mathbf{R})\, \chi_K(\mathbf{R})$) can then be substituted into

$$H(\mathbf{r},\mathbf{R})\, \Psi(\mathbf{r},\mathbf{R}) = E\, \Psi(\mathbf{r},\mathbf{R})$$

$$[H^0 - \hbar^2/2\, \Sigma_{j=1,M}\, m_j^{-1}\, \nabla_j^2 - E]\, \Sigma_K\, \psi_K(\mathbf{r}|\mathbf{R})\, \chi_K(\mathbf{R}) = 0$$

to produce equations for the $\chi_K(\mathbf{R})$ by multiplying by $< \psi_L(\mathbf{r},\mathbf{R})|$ and integrating over $\mathbf{dr}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N$:

$$0 = [E_L(\mathbf{R}) - \hbar^2/2\, \Sigma_{j=1,M}\, m_j^{-1}\, \nabla_j^2 - E]\ \chi_L(\mathbf{R})$$

$$+ \Sigma_K < \psi_L(\mathbf{r}|\mathbf{R})|\ -\hbar^2/2\, \Sigma_{j=1,M}\, m_j^{-1}\, \nabla_j^2\, \psi_K(\mathbf{r}|\mathbf{R})> \chi_K(\mathbf{R})$$

$$+ \Sigma_K < \psi_L(\mathbf{r}|\mathbf{R})|\ -\hbar^2 \Sigma_{j=1,M}\, m_j^{-1}\, \nabla_j\, \psi_K(\mathbf{r}|\mathbf{R})> \bullet \nabla_j\, \chi_K(\mathbf{R})$$

These are called the ***coupled-channel equations***.

If we ignore all of the **non-BO terms**

$$\Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})| -\hbar^2/2 \, \Sigma_{j=1,M} \, m_j^{-1} \, \nabla_j^2 \, \psi_K(\mathbf{r}|\mathbf{R})\rangle \, \chi_K(\mathbf{R})$$

$$+ \Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})| -\hbar^2 \Sigma_{j=1,M} \, m_j^{-1} \, \nabla_j \, \psi_K(\mathbf{r}|\mathbf{R})\rangle \bullet \nabla_j \, \chi_K(\mathbf{R})$$

we obtain a SE for the vib./rot./trans. motion on the L^{th} energy surface $E_L(\mathbf{R})$

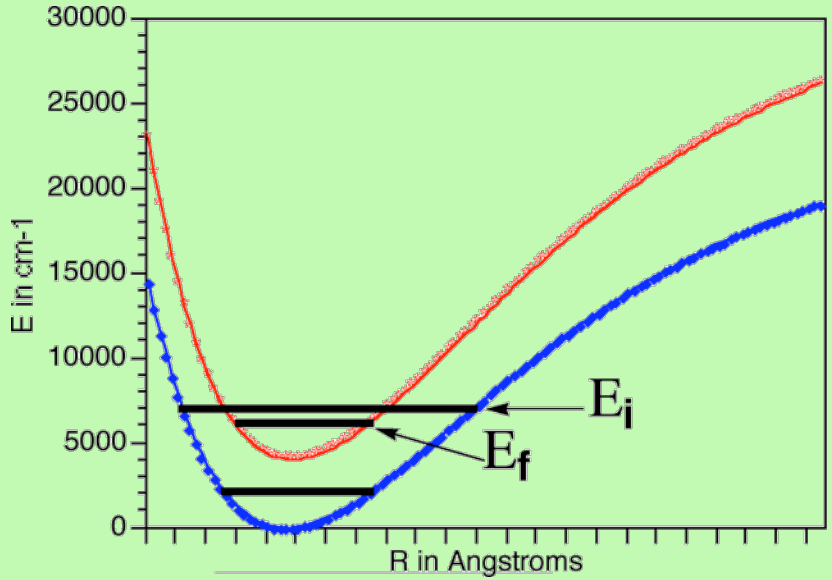
$$0 = [E_L(\mathbf{R}) -\hbar^2/2 \, \Sigma_{j=1,M} \, m_j^{-1} \, \nabla_j^2 \, -E] \;\; \chi_L(\mathbf{R})$$

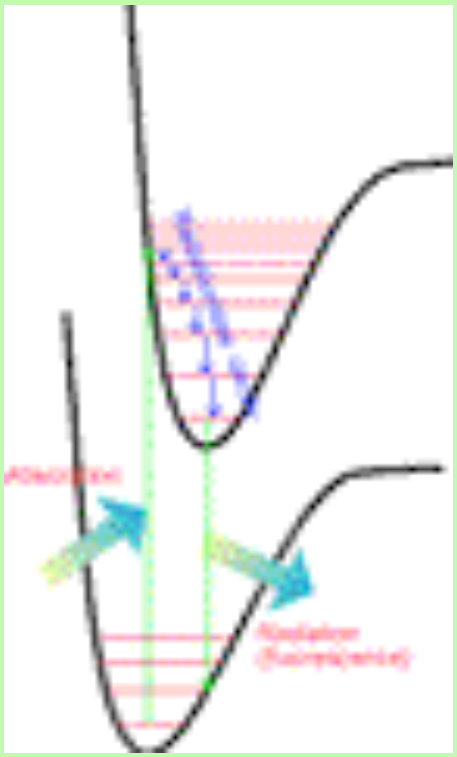
The translational part of $\chi_L(\mathbf{R})$ separates out

(e.g., $\exp(i\mathbf{P}\bullet\mathbf{R}/\hbar)$) and won't be discussed further.

Each electronic state L has its own set of rot./vib. wave functions and energies:

$$[E_L(\mathbf{R}) - \hbar^2/2\, \Sigma_{j=1,M}\, m_j^{-1}\, \nabla_j^2 - E_{L,J,M,\nu}]\ \chi_{L,J,M,\nu}(\mathbf{R}) = 0$$





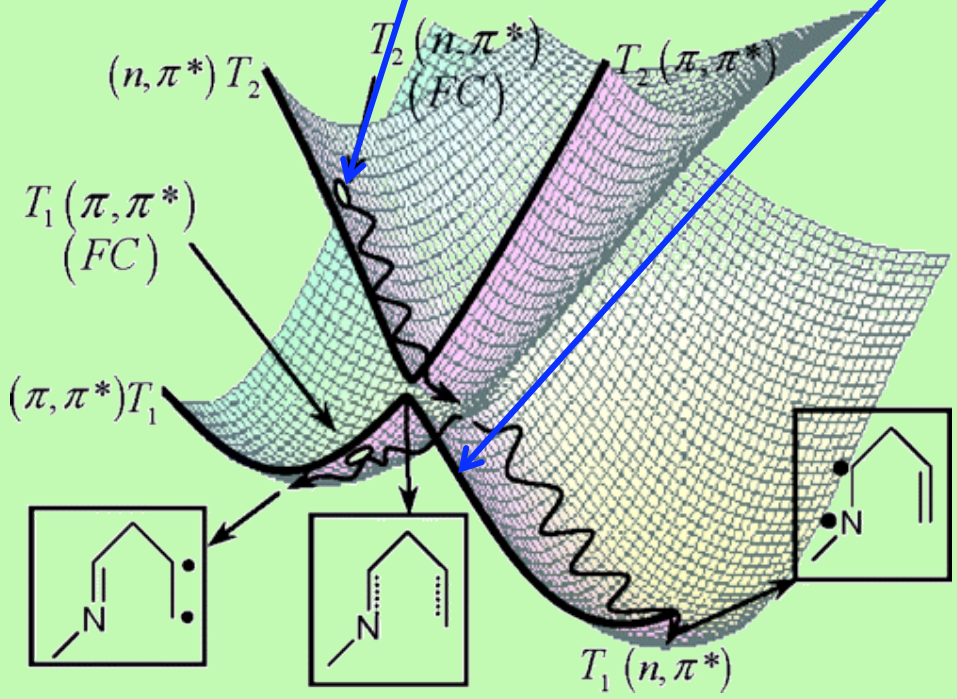
This is the electronic-vibrational-rotational separation one sees in textbooks.

The non-BO couplings

$$\Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})| -\hbar^2/2 \, \Sigma_{j=1,M} \, m_j^{-1} \, \nabla_j^2 \, \psi_K(\mathbf{r}|\mathbf{R})\rangle \, \chi_K(\mathbf{R})$$

$$+ \Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})| -\hbar^2 \Sigma_{j=1,M} \, m_j^{-1} \, \nabla_j \, \psi_K(\mathbf{r}|\mathbf{R})\rangle \bullet \nabla_j \, \chi_K(\mathbf{R})$$

can induce transitions among the BO states (radiationless transitions).



When the nuclear motions are treated classically, these wave functions are replaced by trajectories on the two surfaces.

The expansion $\Psi(\mathbf{r},\mathbf{R}) = \Sigma_K\, \psi_K(\mathbf{r}|\mathbf{R})\, \chi_K(\mathbf{R})$ is replaced by

$$\Psi(\mathbf{r},\mathbf{R}(t)) = \Sigma_K\, c_K(t)\, \psi_K(\mathbf{r}|\mathbf{R}(t))\exp(-i/\hbar \int E_K(\mathbf{R}(t'))dt')$$

and the time-dependent SE

$$H^0(\mathbf{r},\mathbf{R}(t))\, \Psi(\mathbf{r},\mathbf{R}(t)) = i\hbar\, \partial\Psi(\mathbf{r},\mathbf{R}(t))/\partial t$$

is used to derive equations for the $c_K(t)$ amplitudes, assuming the coordinates $\mathbf{R}(t)$ evolve under classical dynamics. The chain rule to

replace $\partial/\partial t\, |\psi_K(\mathbf{r}|\mathbf{R})>$ by $(d\mathbf{R}/dt) \bullet \nabla\, \psi_K(\mathbf{r}|\mathbf{R})>$ gives

$$i\hbar\partial/\partial t\, c_L(t) =$$

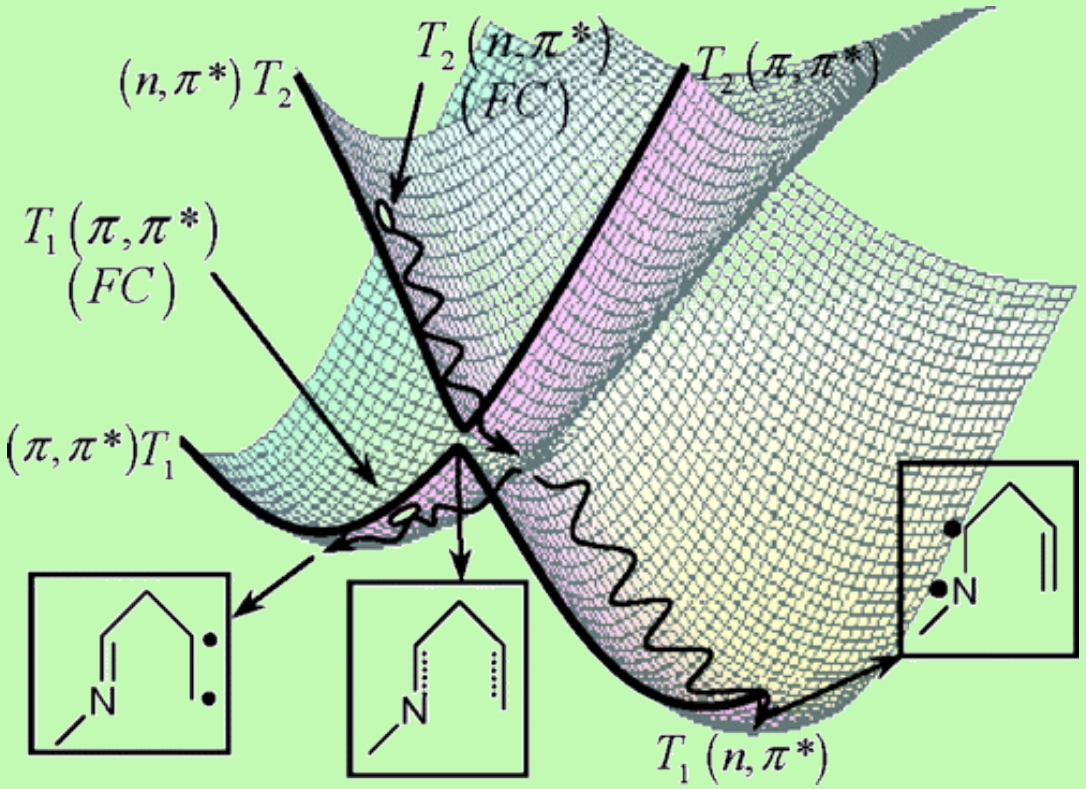
$$-\Sigma_K c_K(t) < \psi_L(\mathbf{r}|\mathbf{R}(t))|\nabla|\psi_K(\mathbf{r}|\mathbf{R}(t))> \bullet (d\mathbf{R}(t)/dt).$$

These coupled equations for the $\{c_L(t)\}$ are solved (as time evolves) as the $\mathbf{R}(t)$ undergo their classical evolution, but one needs to evaluate the non-BO couplings $< \psi_L(\mathbf{r}|\mathbf{R}(t))|\nabla|\psi_K(\mathbf{r}|\mathbf{R}(t))>$ to do so. The values $|c_K(t)|^2$ are used to estimate the probability of being on the K^{th} surface.

The surfaces drawn below are eigenvalues of the electronic SE

$$H^0 \psi_K(\mathbf{r}|\mathbf{R}) = E_K(\mathbf{R}) \psi_K(\mathbf{r}|\mathbf{R})$$

where H^0 contains all but the nuclear kinetic energy. Such surfaces are called adiabatic. Each surface adiabatically evolves as the geometry is changed and T_2 is always above T_1.



Sometimes, one leaves out of H^0 some small terms V (e.g., spin -orbit coupling $A \Sigma_k S_k \bullet L_k$) in defining the BO states. The resulting BO states are called diabatic. One then includes the non -BO couplings

$$\Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})| -\hbar^2/2 \Sigma_{j=1,M} m_j^{-1} \nabla_j^2 \psi_K(\mathbf{r}|\mathbf{R})\rangle \chi_K(\mathbf{R})$$

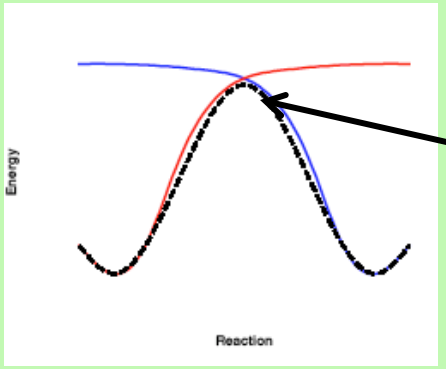
$$+ \Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})| -\hbar^2 \Sigma_{j=1,M} m_j^{-1} \nabla_j \psi_K(\mathbf{r}|\mathbf{R})\rangle \bullet \nabla_j \chi_K(\mathbf{R})$$

$$\mathbf{or} \langle \psi_L(\mathbf{r}|\mathbf{R})|\nabla|\psi_K(\mathbf{r}|\mathbf{R})\rangle$$

as well as couplings

$$\Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})|V|\psi_K(\mathbf{r}|\mathbf{R})\rangle \chi_K(\mathbf{R})$$

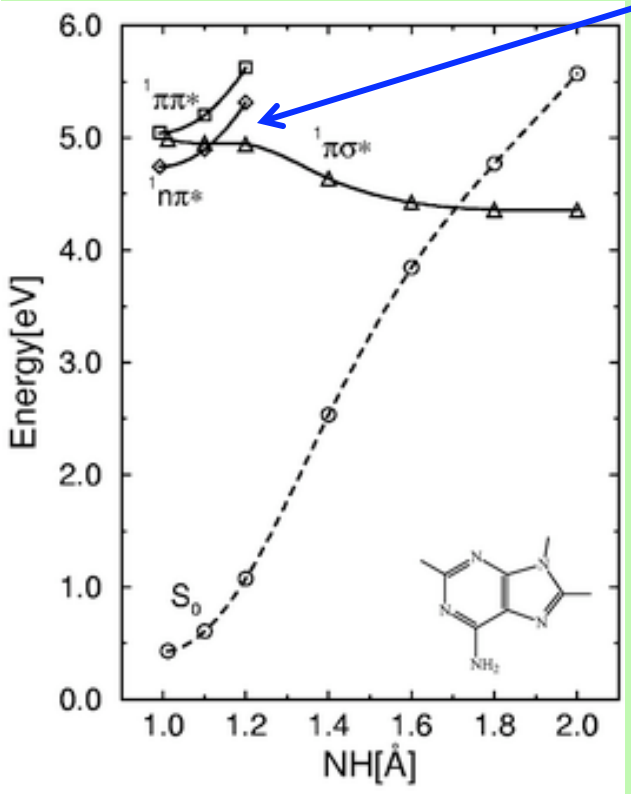
due to the "ignored terms".

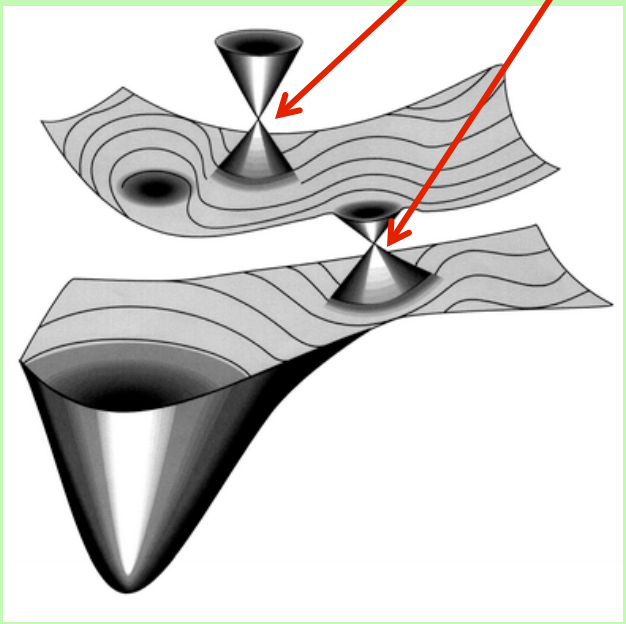


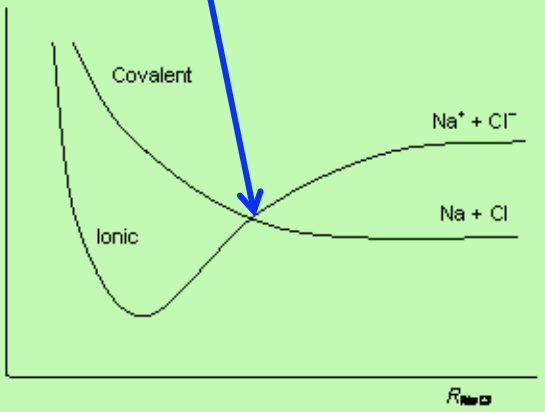
Singlet-triplet diabatic states' curve crossing

Sometimes, one leaves out of H^0 some small terms that couple different electronic configurations (e.g., nπ* or ππ*) in defining the BO states. The resulting BO states are also called diabatic.

At geometries where these diabatic states cross, the couplings $\langle \psi_L(\mathbf{r}|\mathbf{R})|V|\psi_K(\mathbf{r}|\mathbf{R})\rangle$ and $\langle \psi_L(\mathbf{r}|\mathbf{R})|\nabla|\psi_K(\mathbf{r}|\mathbf{R})\rangle$ are especially important to consider.







Again, one includes the non-BO couplings

$$\Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})| -\hbar^2/2 \Sigma_{j=1,M} m_j^{-1} \nabla_j^2 \psi_K(\mathbf{r}|\mathbf{R})\rangle \chi_K(\mathbf{R})$$

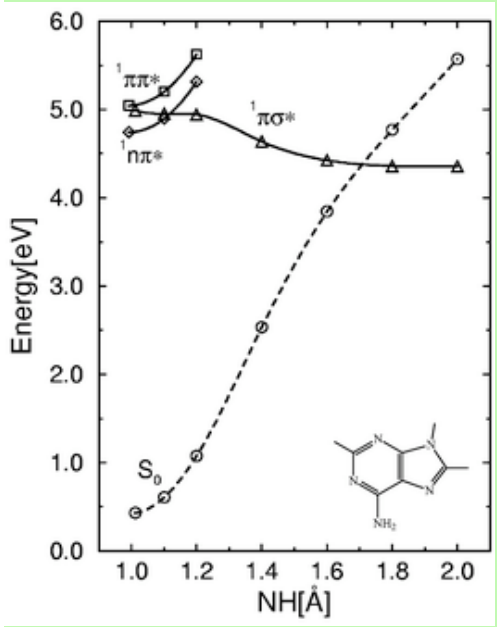
$$+ \Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})| -\hbar^2 \Sigma_{j=1,M} m_j^{-1} \nabla_j \psi_K(\mathbf{r}|\mathbf{R})\rangle \bullet \nabla_j \chi_K(\mathbf{R})$$

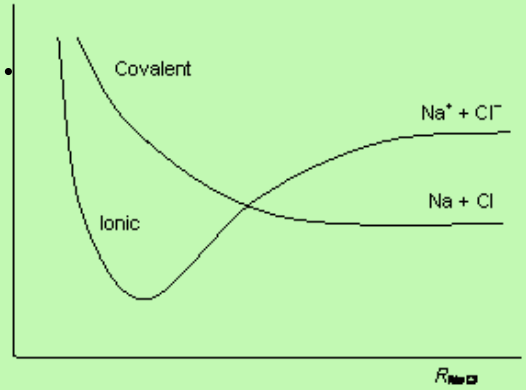
$$\textbf{or} \langle \psi_L(\mathbf{r}|\mathbf{R}(t))|\nabla|\psi_K(\mathbf{r}|\mathbf{R}(t))\rangle$$

as well as couplings

$$\Sigma_K \langle \psi_L(\mathbf{r}|\mathbf{R})|V|\psi_K(\mathbf{r}|\mathbf{R})\rangle \chi_K(\mathbf{R})$$

due to the "ignored terms".





Can adiabatic BO surfaces cross? Suppose that all but two exact BO states have been found and consider two orthogonal functions $\psi_K(\mathbf{r}|\mathbf{R})$ and $\psi_L(\mathbf{r}|\mathbf{R})$ that span the space of the two "missing" exact BO states. Form a 2x2 matrix representation of H^0 within the space spanned by these two functions:

$$\det \begin{vmatrix} \langle\psi_K|H^0|\psi_K\rangle - E & \langle\psi_K|H^0|\psi_L\rangle \\ \langle\psi_L|H^0|\psi_K\rangle & \langle\psi_L|H^0|\psi_L\rangle - E \end{vmatrix} = 0$$

$$E^2 - E(H_{K,K}+H_{L,L}) + H_{K,K}H_{L,L} - H_{K,L}^2 = 0$$

$$E = \tfrac{1}{2}\{(H_{K,K}+H_{L,L}) \pm [(H_{K,K}-H_{L,L})^2 + 4H_{K,L}]^{1/2}\}$$

The two energies can be equal only if both

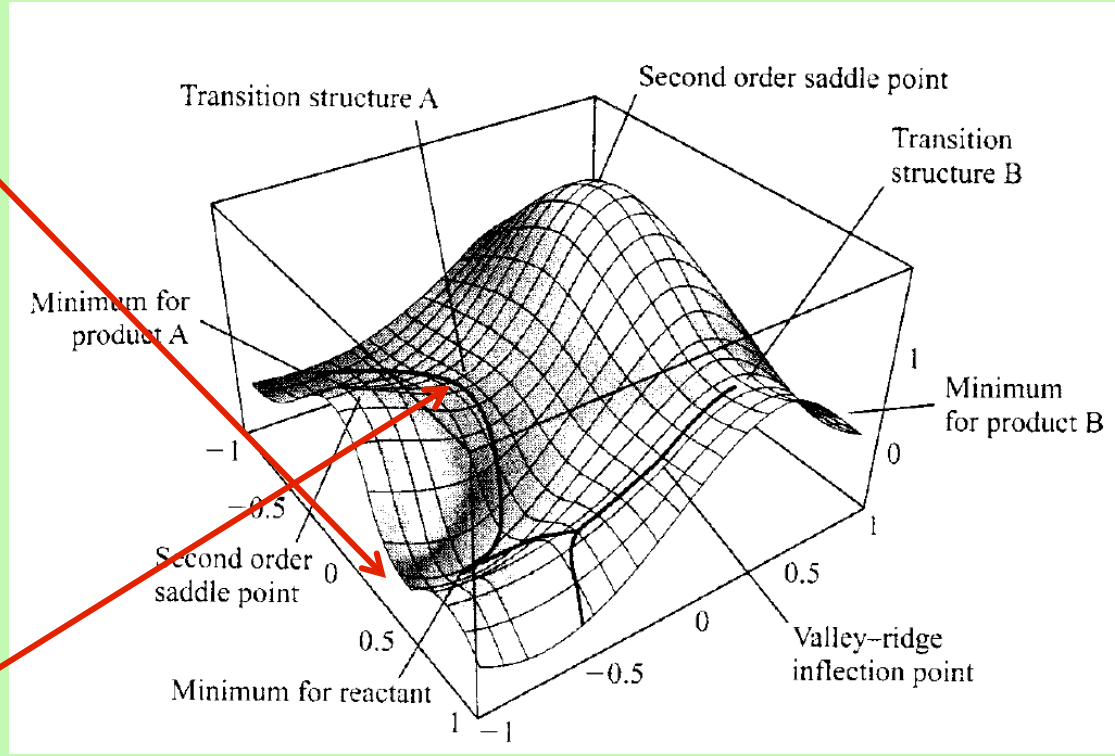
$H_{K,K}(\mathbf{R}) = H_{L,L}(\mathbf{R})$ and

$H_{K,L}(\mathbf{R}) = 0$ at some geometry $\mathbf{R}$.

$\mathbf{R}$ is a 3N-6 dim. space; so the "seam" of intersection is a space of 3N-8 dimensions.

BO energy surfaces have certain critical points to be aware of

Minima (all gradients vanish and all curvatures are positive characteristic of stable geometries



Transition states (all gradients vanish and all but one curvature are positive; one is negative) characteristic of transition states.

Summary: Basic ingredients in BO theory are:

Solve $H^0\ \psi_K(\mathbf{r}|\mathbf{R}) = E_K(\mathbf{R})\ \psi_K(\mathbf{r}|\mathbf{R})$ at specified **R** for states K and L "of interest".
Keep an eye out for geometries $\mathbf{R}^*$ where E_K and E_L intersect or come close.

Solve $[E_L(\mathbf{R}) - \hbar^2/2\ \Sigma_{j=1,M}\ m_j^{-1}\ \nabla_j^2 - E_{L,J,M,\nu}]\ \ \chi_{L,J,M,\nu}(\mathbf{R}) = 0$
or compute classical trajectories **R**(t) on the E_L and E_K surfaces.

Stopping here $\{\Psi(\mathbf{r},\mathbf{R}) = \psi_K(\mathbf{r}|\mathbf{R})\ \chi_K(\mathbf{R})$ or $\Psi(\mathbf{r},\mathbf{R}) = \psi_L(\mathbf{r}|\mathbf{R})\ \chi_L(\mathbf{R})\}$ = pure BO

To go beyond the BO approximation, compute all of the couplings:

$\Sigma_K < \psi_L(\mathbf{r}|\mathbf{R})|\ -\hbar^2/2\ \Sigma_{j=1,M}\ m_j^{-1}\ \nabla_j^2\ \psi_K(\mathbf{r}|\mathbf{R})>\ \chi_K(\mathbf{R})$

$+\ \Sigma_K < \psi_L(\mathbf{r}|\mathbf{R})|\ -\hbar^2 \Sigma_{j=1,M}\ m_j^{-1}\ \nabla_j\ \psi_K(\mathbf{r}|\mathbf{R})>\ \bullet\nabla_j\ \chi_K(\mathbf{R})$

$\Sigma_K < \psi_L(\mathbf{r}|\mathbf{R})|V|\psi_K(\mathbf{r}|\mathbf{R})>\ \chi_K(\mathbf{R})$ (or $< \psi_L(\mathbf{r}|\mathbf{R}(t))|\nabla|\psi_K(\mathbf{r}|\mathbf{R}(\mathbf{t}))>$) and

evaluate the effects of the couplings on the nuclear-motion state $\chi_L(\mathbf{R})$ or on the

classical trajectory coupling surface $E_L(\mathbf{R})$ to $E_K(\mathbf{R})$. How is this done?