

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

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

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

$|\Psi(\mathbf{r},\mathbf{R})|^2$ gives probability density for finding electrons at $\mathbf{r} = \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N$ and nuclei at $\mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3 \dots \mathbf{R}_M$.

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

nuclear kinetic energy $T_M = -\hbar^2/2 \sum_{j=1,M} m_j^{-1} \nabla_j^2$

electron-nuclei Coulomb potentials $- \sum_{j=1,M} Z_j \sum_{k=1,N} e^2 / |\mathbf{r}_k - \mathbf{R}_j|$

V_{eM} nuclear-nuclear Coulomb repulsions $\sum_{j<k=1,M} Z_j Z_k e^2 / |\mathbf{R}_k - \mathbf{R}_j|$

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

It can contain more terms if, for example, external electric or magnetic fields are present (e.g., $\sum_{k=1,N} e \mathbf{r}_k \bullet \mathbf{E}$).

In the **Born-Oppenheimer** approximation/separation, we ignore the T_M motions of the nuclei (pretend the nuclei are fixed at specified locations \mathbf{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**. H^0 contains all of H except T_M .

Because H^0 is Hermitian, its eigenfunctions form a complete set of functions of \mathbf{r} . So, the full Ψ can be expanded in the ψ_K :

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

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

$$- \sum_{j=1, M} Z_j \sum_{k=1, N} e^2 / |\mathbf{r}_k - \mathbf{R}_j| .$$

This expansion can then be used in

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

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

to produce equations for the $\chi_K(\mathbf{R})$:

$$\begin{aligned} 0 &= [E_L(\mathbf{R}) - \hbar^2/2 \sum_{j=1, M} m_j^{-1} \nabla_j^2 - E] \chi_L(\mathbf{R}) \\ &+ \sum_K \langle \psi_L(\mathbf{r}, \mathbf{R}) | -\hbar^2/2 \sum_{j=1, M} m_j^{-1} \nabla_j^2 \psi_K(\mathbf{r}, \mathbf{R}) \rangle \chi_K(\mathbf{R}) \\ &+ \sum_K \langle \psi_L(\mathbf{r}, \mathbf{R}) | -\hbar^2 \sum_{j=1, M} m_j^{-1} \nabla_j \psi_K(\mathbf{r}, \mathbf{R}) \rangle \bullet \nabla_j \chi_K(\mathbf{R}) \end{aligned}$$

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

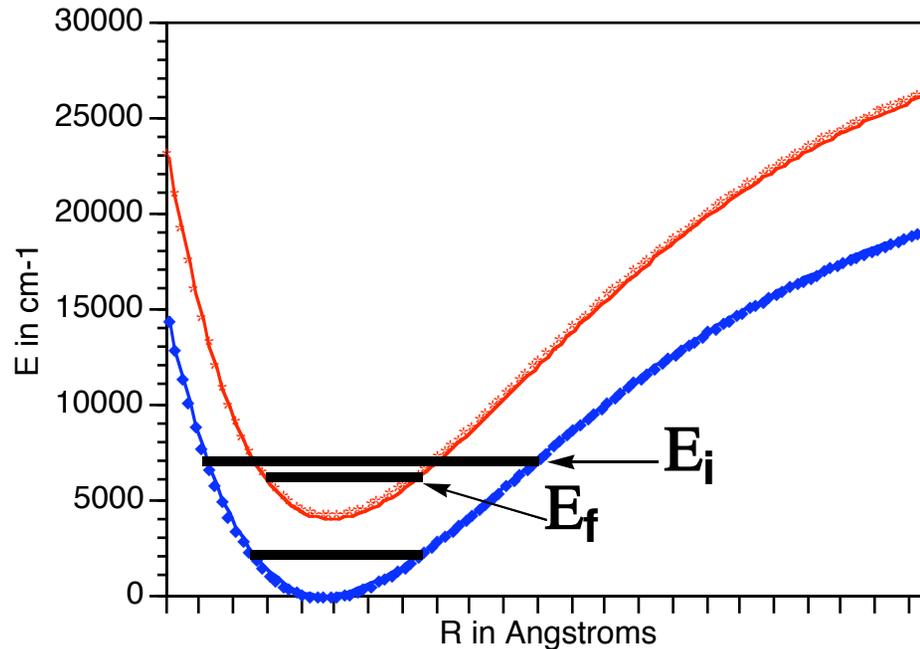
If we ignore all of the **non-adiabatic terms**, we obtain a SE

For the vib./rot./trans. Motion

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

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

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



The non-adiabatic couplings can induce transitions among these states (radiationless transitions).

There are **major difficulties in solving the electronic SE:**

V_{ee} makes the equation **not separable**- this means ψ is not rigorously a product of functions of individual electron coordinates.

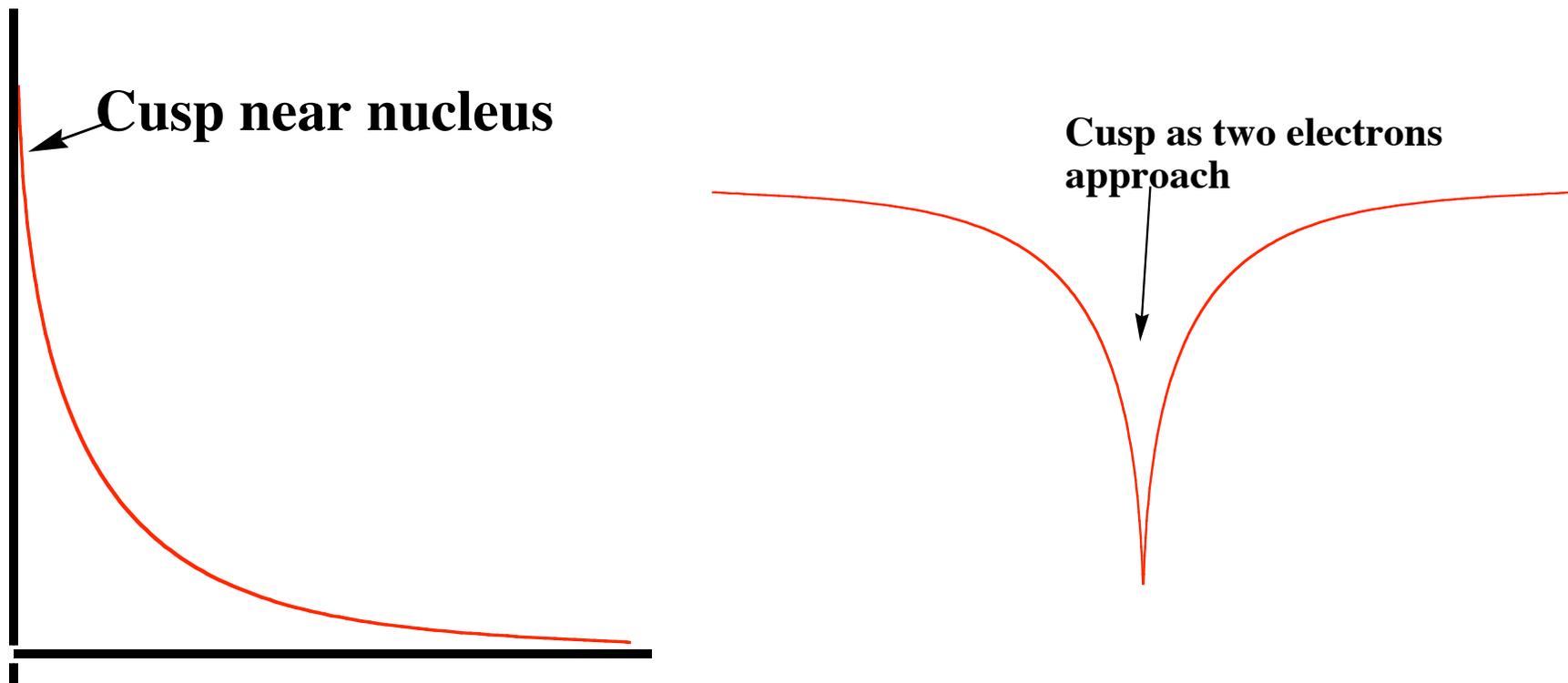
$\psi \neq \phi_1 \phi_2 \phi_3 \phi_4 \phi_5$ (e.g., $1s\alpha(1) 1s\beta(2) 2s\alpha(3) 2s\beta(4) 2p1\alpha(5)$)

Cusps

The factors $(1/r_k \partial/\partial r_k - Ze^2/r_k) \psi$ and $(1/r_{k,l} \partial/\partial r_{k,l} + e^2/r_{k,l}) \psi$

will blow up unless so-called **cusp conditions** are obeyed by ψ :

$\partial/\partial r_k \psi = Ze^2 \psi$ (as $r_k \rightarrow 0$) and $\partial/\partial r_{k,l} \psi = -e^2 \psi$ (as $r_{k,l} \rightarrow 0$).



This means when we try to approximately solve the electronic SE, we should use trial functions that have such cusps. Slater-type orbitals ($\exp(-\zeta r)$) have cusps at nuclei, but Gaussians ($\exp(-\alpha r^2)$) do not. We rarely use functions with e-e cusps, but we should.

Addressing the **non-separability** problem:

If V_{ee} could be replaced by a one-electron additive potential

$$V_{MF} = \sum_{j=1,N} V_{MF}(\mathbf{r}_j)$$

the solutions ψ would be products (actually antisymmetrized products called Slater determinants) of functions of individual electron coordinates (spin-orbitals):

$$\psi = | \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \phi_3(\mathbf{r}_3) \phi_4(\mathbf{r}_4) \phi_5(\mathbf{r}_5) |$$

$$= (N!)^{-1/2} \sum_{P=1,N!} P \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \phi_3(\mathbf{r}_3) \phi_4(\mathbf{r}_4) \phi_5(\mathbf{r}_5)$$

Before considering finding a V_{MF} , let's examine how important antisymmetry is by considering two electrons in π and π^* orbitals.

Singlet π^2 $|\pi\alpha(1) \pi\beta(2)| = 2^{-1/2} \pi(1)\pi(2)[\alpha_1\beta_2 - \beta_1\alpha_2]$

Triplet $\pi\pi^*$ $|\pi\alpha(1) \pi^*\alpha(2)| = 2^{-1/2} [\pi(1)\pi^*(2) - \pi(2)\pi^*(1)] \alpha_1\alpha_2$

$|\pi\beta(1) \pi^*\beta(2)| = 2^{-1/2} [\pi(1)\pi^*(2) - \pi(2)\pi^*(1)] \beta_1\beta_2$

$2^{-1/2} [|\pi\alpha(1) \pi^*\beta(2)| + |\pi\beta(1) \pi^*\alpha(2)|] =$

$2^{-1} [\pi(1)\pi^*(2)\alpha_1\beta_2 + \pi(1)\pi^*(2)\beta_1\alpha_2$

$-\pi^*(1)\pi(2)\beta_1\alpha_2 - \pi^*(1)\pi(2)\alpha_1\beta_2]$

Singlet $\pi\pi^*$ $2^{-1/2} [|\pi\alpha(1) \pi^*\beta(2)| - |\pi\beta(1) \pi^*\alpha(2)|] =$

$2^{-1} [\pi(1)\pi^*(2)\alpha_1\beta_2 - \pi(1)\pi^*(2)\beta_1\alpha_2$

$-\pi^*(1)\pi(2)\beta_1\alpha_2 + \pi^*(1)\pi(2)\alpha_1\beta_2]$

Singlet π^{*2} $|\pi^*\alpha(1) \pi^*\beta(2)| = 2^{-1/2} \pi^*(1)\pi^*(2)[\alpha_1\beta_2 - \beta_1\alpha_2]$

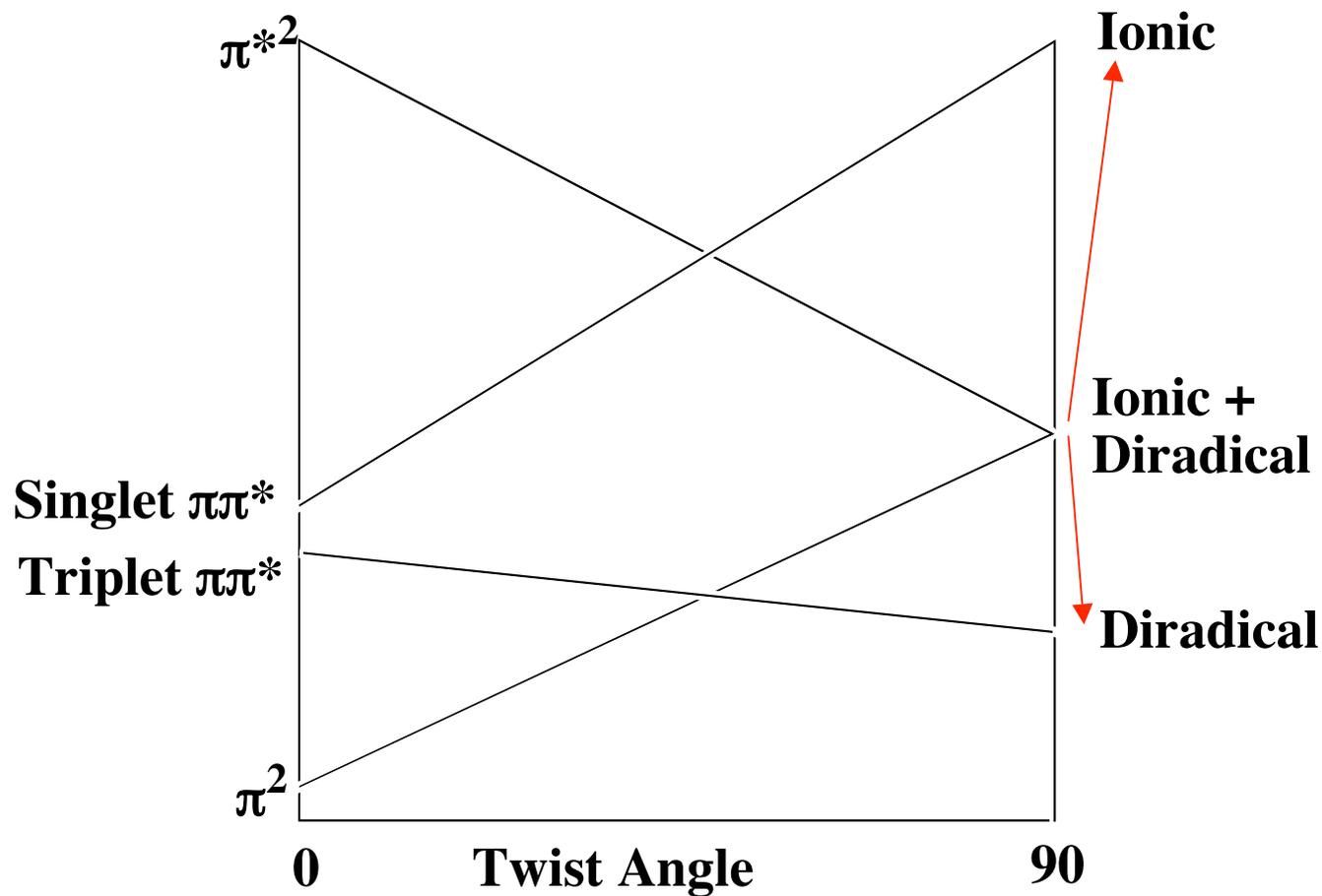
Now think of $\pi = 2^{-1/2} (L + R)$ and $\pi^* = 2^{-1/2} (L - R)$

$$|\pi\alpha(1) \pi\beta(2)| = 2^{-1}[|\mathbf{R}\alpha(1) \mathbf{R}\beta(2)| + |\mathbf{L}\alpha(1) \mathbf{L}\beta(2)| + |\mathbf{R}\alpha(1) \mathbf{L}\beta(2)| + |\mathbf{L}\alpha(1) \mathbf{R}\beta(2)|] \quad \text{ionic + diradical}$$

$$|\pi^*\alpha(1) \pi^*\beta(2)| = 2^{-1}[|\mathbf{R}\alpha(1) \mathbf{R}\beta(2)| + |\mathbf{L}\alpha(1) \mathbf{L}\beta(2)| - |\mathbf{R}\alpha(1) \mathbf{L}\beta(2)| - |\mathbf{L}\alpha(1) \mathbf{R}\beta(2)|] \quad \text{ionic + diradical}$$

$$2^{-1/2} [|\pi\alpha(1) \pi^*\beta(2)| - |\pi\beta(1) \pi^*\alpha(2)|] = 2^{-3/2} [|\mathbf{R}\alpha(1) \mathbf{R}\beta(2)| + |\mathbf{L}\alpha(1) \mathbf{R}\beta(2)| - |\mathbf{R}\alpha(1) \mathbf{L}\beta(2)| - |\mathbf{L}\alpha(1) \mathbf{L}\beta(2)|] - 2^{-3/2} [|\mathbf{R}\beta(1) \mathbf{R}\alpha(2)| + |\mathbf{L}\beta(1) \mathbf{R}\alpha(2)| - |\mathbf{R}\beta(1) \mathbf{L}\alpha(2)| - |\mathbf{L}\beta(1) \mathbf{L}\alpha(2)|] = 2^{-1/2} [|\mathbf{R}\alpha(1) \mathbf{R}\beta(2)| + |\mathbf{L}\alpha(1) \mathbf{R}\beta(2)|] \quad \text{ionic}$$

$$|\pi\alpha(1) \pi^*\alpha(2)| = 2^{-1}[|\mathbf{L}\alpha(1) \mathbf{R}\alpha(2)| - |\mathbf{R}\alpha(1) \mathbf{L}\alpha(2)|] = |\mathbf{L}\alpha(1) \mathbf{R}\alpha(2)| \quad \text{diradical}$$



To adequately describe the π^2 bond breaking, we need to mix the π^2 and π^{*2} **configuration state functions (CSF)**. This shows how single configuration functions may not be adequate.

$$|\pi\alpha(1) \pi\beta(2)\rangle = 2^{-1}[|R\alpha(1) R\beta(2)\rangle + |L\alpha(1) L\beta(2)\rangle + |R\alpha(1) L\beta(2)\rangle + |L\alpha(1) R\beta(2)\rangle] \quad \text{ionic + diradical}$$

$$|\pi^*\alpha(1) \pi^*\beta(2)\rangle = 2^{-1}[|R\alpha(1) R\beta(2)\rangle + |L\alpha(1) L\beta(2)\rangle - |R\alpha(1) L\beta(2)\rangle - |L\alpha(1) R\beta(2)\rangle] \quad \text{ionic + diradical}$$

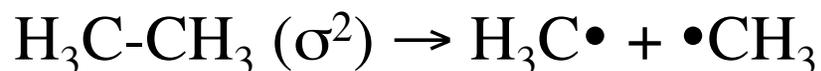
So, one must combine $2^{-1/2}\{|\pi\alpha(1) \pi\beta(2)\rangle - |\pi^*\alpha(1) \pi^*\beta(2)\rangle\}$

to obtain a diradical state and

$$2^{-1/2}\{|\pi\alpha(1) \pi\beta(2)\rangle + |\pi^*\alpha(1) \pi^*\beta(2)\rangle\}$$

to obtain an ionic state.

Analogous “trouble” occurs whenever one uses a single determinant HF wave function to describe a bond that one wants to break:



As we will see soon, one can partially solve this problem by using a so-called unrestricted HF (UHF) wave function, but it has problems as well.

How does one find a V_{MF} ? One way is to postulate that

$$\psi = |\phi_1 \phi_2 \phi_3 \dots \phi_N|,$$

and write down $\langle \psi | H | \psi \rangle$ using the **Slater-Condon rules**:

$$\langle \psi | H | \psi \rangle = \sum_k \langle \phi_k | T_e + V_{e,n} + V_{n,n} | \phi_k \rangle + 1/2 \sum_{k,l}$$

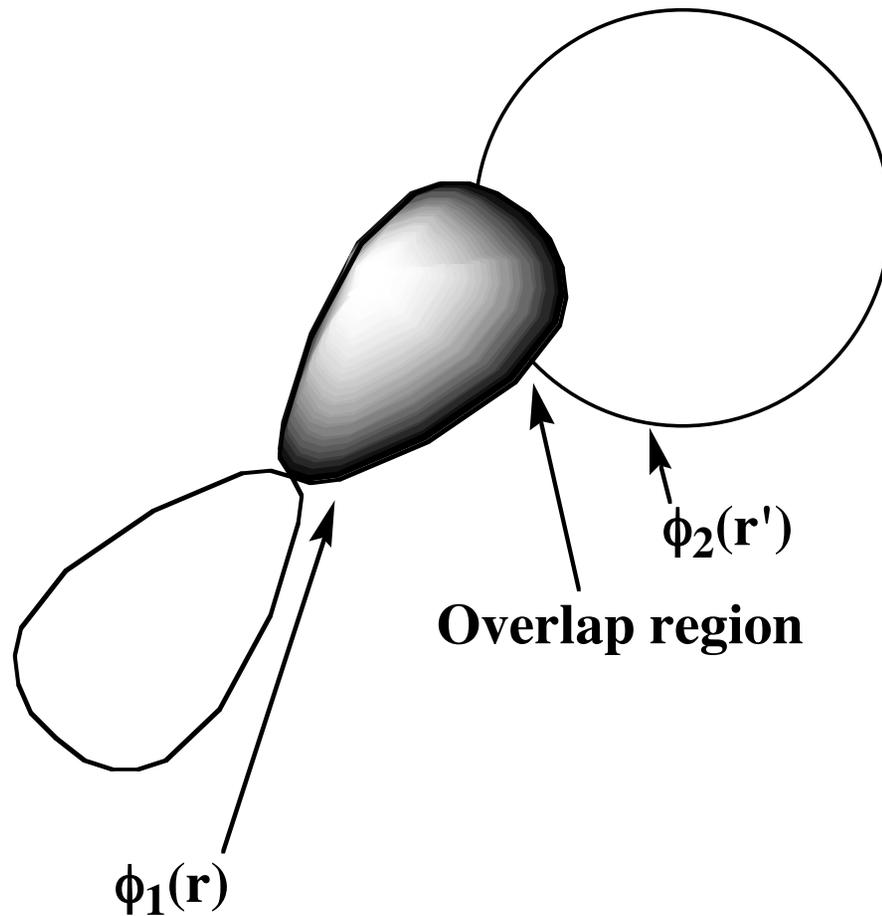
$$[\langle \phi_k(1) \phi_l(2) | e^2/r_{1,2} | \phi_k(1) \phi_l(2) \rangle - \langle \phi_k(1) \phi_l(2) | e^2/r_{1,2} | \phi_l(1) \phi_k(2) \rangle]$$

and observe that Coulomb (J) and exchange (K) interactions among spin-orbitals arise. If one also minimizes this energy with respect to the ϕ 's, one obtains equations $h \phi_J = \varepsilon_J \phi_J = [T_e + V_{e,n} + V_{n,n}] \phi_J + \sum_k [\langle \phi_k(1) | e^2/r_{1,2} | \phi_k(1) \rangle \phi_J(2) - \langle \phi_k(1) | e^2/r_{1,2} | \phi_J(1) \rangle \phi_k(2)]$.

that contain the J and K potentials.

$$J_{1,2} = \int |\phi_1(\mathbf{r})|^2 \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\phi_2(\mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}'$$

$$K_{1,2} = \int \phi_1(\mathbf{r}) \phi_2(\mathbf{r}') \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_2(\mathbf{r}) \phi_1(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$



So, one is motivated to define V_{MF} in terms of the J and K interactions. This is the **Hartree-Fock** definition of V_{MF} . It has the characteristic that $\langle \psi | H | \psi \rangle = \langle \psi | H^0 | \psi \rangle$, so if $H - H^0$ is viewed as a perturbation and H^0 is defined as

$$H^0 = T_e + V_{e,n} + V_{n,n} + (J-K)$$

there is no first-order perturbation correction to the energy. This choice of H^0 forms the basis of **Møller-Plesset** perturbation theory (**MPn**).

It is by making a mean-field model that our (chemists') concepts of orbitals and of electronic configurations (e.g., $1s \alpha 1s \beta 2s \alpha 2s \beta 2p_1 \alpha$) arise.

Another good thing about HF orbitals is that their energies ϵ_K give approximate ionization potentials and electron affinities (**Koopmans' theorem**). This can be shown by writing down the energies of two Slater determinants

$$\psi_0 = |\phi_1 \phi_2 \phi_3 \dots \phi_N| \text{ and } \psi_- = |\phi_1 \phi_2 \phi_3 \dots \phi_N \phi_{N+1}|,$$

using the energy expression $\sum_k \langle \phi_k | T_e + V_{e,n} + V_{n,n} | \phi_k \rangle + 1/2 \sum_{k,l}$

$$[\langle \phi_k(1) \phi_l(2) | e^2/r_{1,2} | \phi_k(1) \phi_l(2) \rangle - \langle \phi_k(1) \phi_l(2) | e^2/r_{1,2} | \phi_l(1) \phi_k(2) \rangle]$$

and subtracting the two energy expressions to obtain the energy difference. You try it as a **homework problem** and see if you can show the energy difference is indeed ϵ_{N+1} .

The sum of the orbital energies is not equal to the HF energy:

$$E = \sum_k \langle \phi_k | T_e + V_{e,n} + V_{n,n} | \phi_k \rangle + \frac{1}{2} \sum_{k,l}$$

$$[\langle \phi_k(1) \phi_l(2) | e^2/r_{1,2} | \phi_k(1) \phi_l(2) \rangle - \langle \phi_k(1) \phi_l(2) | e^2/r_{1,2} | \phi_l(1) \phi_k(2) \rangle]$$

$$\varepsilon_k = \langle \phi_k | T_e + V_{e,n} + V_{n,n} | \phi_k \rangle + \sum_l$$

$$[\langle \phi_k(1) \phi_l(2) | e^2/r_{1,2} | \phi_k(1) \phi_l(2) \rangle - \langle \phi_k(1) \phi_l(2) | e^2/r_{1,2} | \phi_l(1) \phi_k(2) \rangle]$$

The Brillouin theorem holds:

$$\langle \phi_1 \phi_2 \phi_a \dots \phi_N | H | \phi_1 \phi_2 \phi_m \dots \phi_N \rangle = \langle \phi_a | T_e + V_{e,n} + V_{n,n} | \phi_m \rangle + \sum_l$$

$$[\langle \phi_a(1) \phi_l(2) | e^2/r_{1,2} | \phi_m(1) \phi_l(2) \rangle - \langle \phi_a(1) \phi_l(2) | e^2/r_{1,2} | \phi_l(1) \phi_m(2) \rangle]$$

$$= \langle \phi_a | h_{\text{HF}} | \phi_m \rangle = 0$$

The Slater-Condon rules- memorize them

(i) If $| \rangle$ and $|' \rangle$ are identical, then

$$\langle | F + G | \rangle =$$

$$\sum_i \langle \phi_i | f | \phi_i \rangle + \sum_{i>j} [\langle \phi_i \phi_j | g | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | g | \phi_j \phi_i \rangle],$$

where the sums over i and j run over all spin-orbitals in $| \rangle$;

(ii) If $| \rangle$ and $|' \rangle$ differ by a single spin-orbital ($\phi_p \neq \phi'_p$),

$$\langle | F + G |' \rangle =$$

$$\langle \phi_p | f | \phi'_p \rangle + \sum_j [\langle \phi_p \phi_j | g | \phi'_p \phi_j \rangle - \langle \phi_p \phi_j | g | \phi_j \phi'_p \rangle],$$

where the sum over j runs over all spin-orbitals in $| \rangle$ except ϕ_p ;

(iii) If $| \rangle$ and $|' \rangle$ differ by two ($\phi_p \neq \phi'_p$ and $\phi_q \neq \phi'_q$),

$$\langle | F + G |' \rangle =$$

$$\langle \phi_p \phi_q | g | \phi'_p \phi'_q \rangle - \langle \phi_p \phi_q | g | \phi'_q \phi'_p \rangle$$

(note that the F contribution vanishes in this case);

(iv) If $| \rangle$ and $|' \rangle$ differ by three or more spin orbitals, then

$$\langle | F + G |' \rangle = 0;$$

(v) For the identity operator I , $\langle | I |' \rangle = 0$ if $| \rangle$ and $|' \rangle$ differ by one or more spin-orbitals.

Some single-configuration functions are not single determinants.

There are cases where more than one determinant must be used.

Although the determinant $|1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_z\alpha\ 2p_y\alpha|$ is an acceptable approximation to the carbon 3P state if the $1s$ and $2s$ spin-orbitals are restricted to be equal for α and β spins, the 1S state arising in this same $1s^2 2s^2 2p^2$ configuration can not be represented as a single determinant. The 1S state requires a minimum of the following three-determinant wave function:

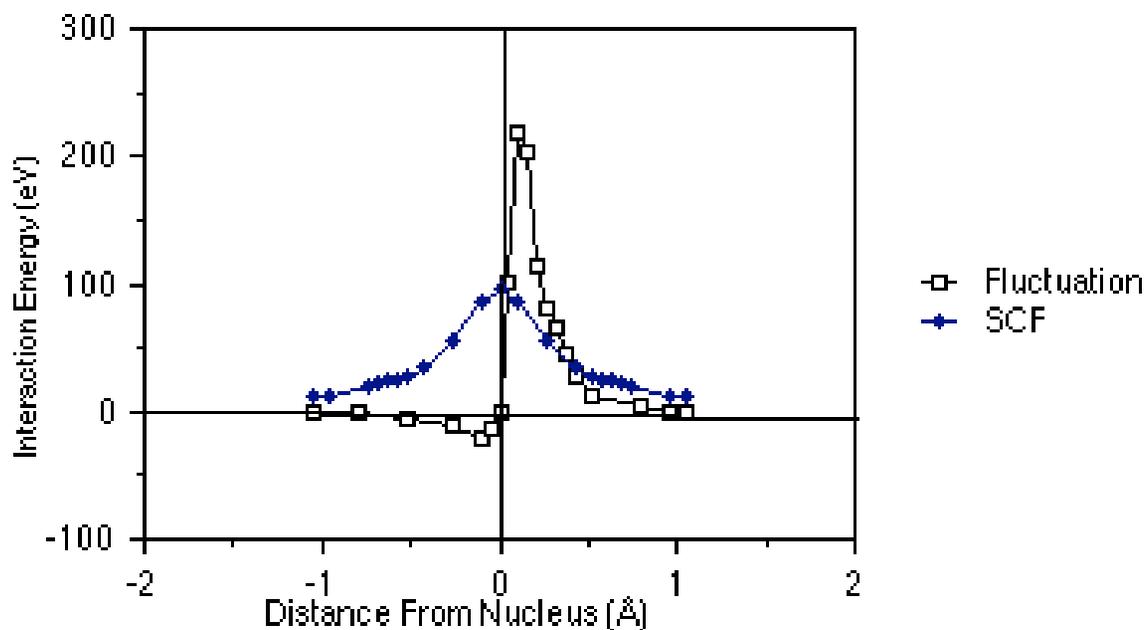
$$\Psi = 3^{-1/2} [1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_z\alpha\ 2p_z\beta|$$

$$- 1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_x\alpha\ 2p_x\beta| - 1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_y\alpha\ 2p_y\beta|] .$$

If a state cannot be represented by a single determinant, one should not use theoretical methods that are predicated on a dominant single determinant in the expansion of the full wave function.

We have dealt with the non-separability issue, but what about the **cusps**? Is doing so necessary? Yes it is!

Example- carbon atom's total electronic energy is -1030.080 eV and $J_{2p_x, 2p_y} = 13$ eV, so the J's (and K's) are large quantities on a "chemical" scale of 1 kcal/mol. The Be 1s/1s interaction in the HF approximation and in reality differ a lot.



So, the electron-electron interactions are large quantities and the errors made in describing them in terms of the HF mean-field picture are also large.

Why don't we use ψ functions that have electron-electron cusps? Sometimes we do (explicitly correlated wave functions are used in so-called **r-12 methods**), but this results in very difficult theories to implement and very computer-intensive calculations. We'll hear more later from Martin Head-Gordon about this.

The most common way to improve beyond the HF $|\phi_1 \phi_2 \phi_3 \dots \phi_N\rangle$ is to use trial wave functions of the so-called **configuration interaction (CI)** form $\psi = \sum_L C_{L1,L2,\dots,LN} |\phi_{L1} \phi_{L2} \phi_{L3} \dots \phi_{LN}\rangle$. This makes mathematical sense because the determinants $|\phi_{L1} \phi_{L2} \phi_{L3} \dots \phi_{LN}\rangle$ form orthonormal complete sets, so ψ can be so expanded. Physically, what does this mean? Here is a useful identity for two determinants that one can use to interpret such CI wave functions:

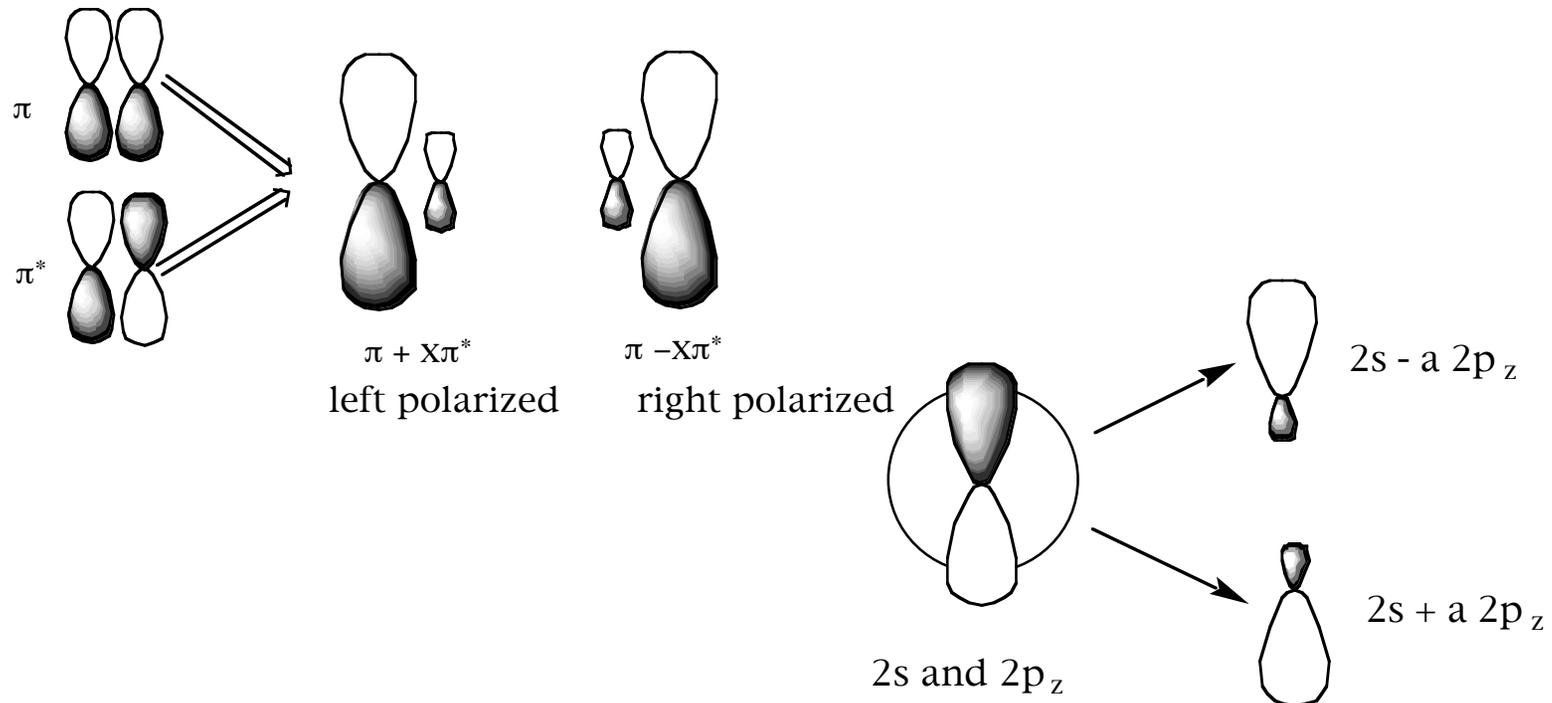
$$\Psi = C_1 | \dots \phi_\alpha \phi_\beta \dots \rangle - C_2 | \dots \phi'_\alpha \phi'_\beta \dots \rangle$$

$$= C_1/2 \{ | \dots (\phi - x\phi')_\alpha (\phi + x\phi')_\beta \dots \rangle - | \dots (\phi - x\phi')_\beta (\phi + x\phi')_\alpha \dots \rangle \}.$$

with $x = (C_2/C_1)^{1/2}$

So a combination of two determinants that differ by doubly occupied orbital ϕ being replaced by doubly occupied ϕ' is equivalent to **singlet $2^{-1/2} (\alpha\beta - \beta\alpha)$ coupled polarized orbital pairs** $\phi - x\phi'$ and $\phi + x\phi'$.

For example $\pi^2 \rightarrow \pi^{*2}$ CI in olefins or $2s^2 \rightarrow 2p^2$ CI in alkaline earth atoms produce the following polarized orbital pairs.



Placing electrons into different polarized orbital pairs allows them to avoid one another and thus correlate their motions. This correlation is how the wave functions attempt to approach the e-e **cusp condition**.

Sometimes the CI is **essential**- for example, to adequately describe breaking the π bond in the singlet state of an olefin. However, CI is always important if one wishes to include electron-electron avoidance that is called **dynamical correlation**.

In all cases, it is useful to keep in mind the polarized orbital pair model:

$$\Psi = C_1 | \dots \phi_\alpha \phi_\beta \dots | - C_2 | \dots \phi'_\alpha \phi'_\beta \dots |$$

$$= C_1/2 \{ | \dots (\phi - x\phi')_\alpha (\phi + x\phi')_\beta \dots | - | \dots (\phi - x\phi')_\beta (\phi + x\phi')_\alpha \dots | \}$$

Let's get a bit more specific. How does one determine the orbitals ϕ_J and then how does one determine the CI coefficients C_J ?

The orbitals are usually determined by carrying out a **HF calculation**. This is not done (except in rare cases) by solving the HF differential equations on a spatial grid but by expanding the ϕ_J in terms of so-called atomic orbital (AO) (because they usually are centered on atoms) **basis functions**- the **LCAO-MO** expansion:

$$\phi_J = \sum_{\mu} \chi_{\mu} C_{J,\mu}$$

This reduces the HF calculation to a matrix eigenvalue form

$$\sum_{\mu} \langle \chi_{\nu} | h_e | \chi_{\mu} \rangle C_{J,\mu} = \epsilon_J \sum_{\mu} \langle \chi_{\nu} | \chi_{\mu} \rangle C_{J,\mu}$$

The matrix elements needed to carry out such a calculation are

$$\begin{aligned}
 \langle \chi_\nu | h_e | \chi_\mu \rangle &= \langle \chi_\nu | -\hbar^2/2m \nabla^2 | \chi_\mu \rangle + \sum_a \langle \chi_\nu | -Z_a e^2/r_a | \chi_\mu \rangle \\
 &+ \sum_K C_{K,\eta} C_{K,\gamma} [\langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\mu(r) \chi_\gamma(r') \rangle \\
 &- \langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\gamma(r) \chi_\mu(r') \rangle] \text{ and the overlap integrals} \\
 &\langle \chi_\nu | \chi_\mu \rangle.
 \end{aligned}$$

The number of these one- and two electron integrals scales with the basis set size M as M^2 and M^4 . The computer effort needed to solve the $M \times M$ eigenvalue problem scales as M^3 . The sum over K runs over all of the **occupied spin-orbitals**.

UHF Wavefunctions are not eigenfunctions of S^2

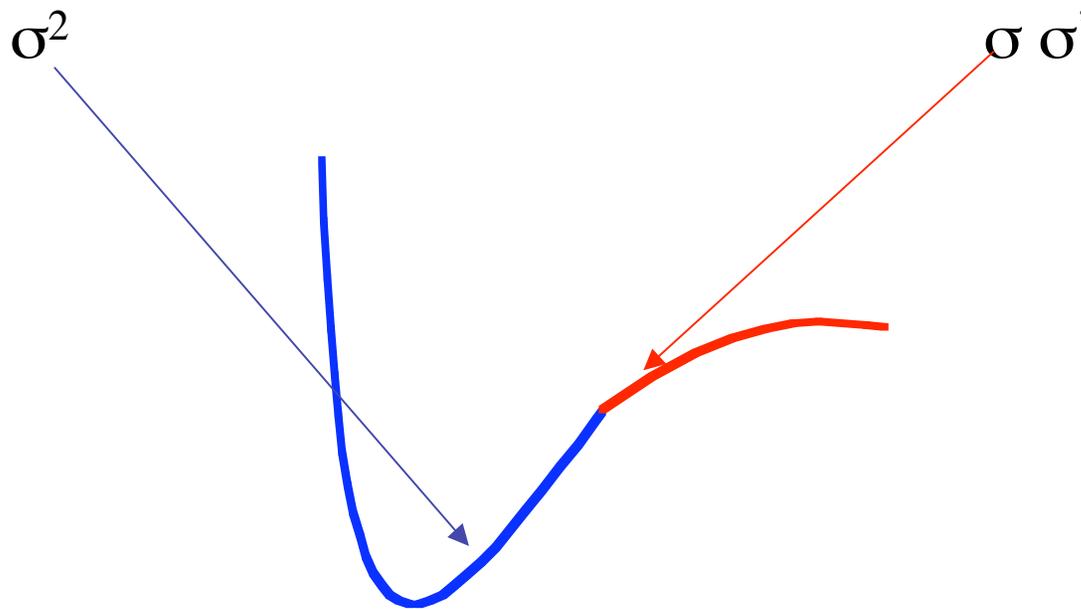
$$\begin{aligned} \langle \chi_\nu | h_e | \chi_\mu \rangle &= \langle \chi_\nu | -\hbar^2/2m \nabla^2 | \chi_\mu \rangle + \sum_a \langle \chi_\nu | -Z_a e^2/r_a | \chi_\mu \rangle \\ &+ \sum_K C_{K,\eta} C_{K,\gamma} [\langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\mu(r) \chi_\gamma(r') \rangle \\ &- \langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\gamma(r) \chi_\mu(r') \rangle]. \end{aligned}$$

The matrix elements of the Fock operator are different for an α and a β spin-orbital because the sum $\sum_K C_{K,\eta} C_{K,\gamma}$ appearing in these matrix elements runs over all N of the occupied spin-orbitals. If the spin-orbital being solved for is of α type, there will be Coulomb integrals for $K = 1s\alpha, 1s\beta, 2s\alpha, 2s\beta, 2p_z\alpha,$ and $2p_y\alpha$ and exchange contributions for $K = 1s\alpha, 2s\alpha, 2p_z\alpha,$ and $2p_y\alpha$. On the other hand, when solving for spin-orbitals of β type, there will be Coulomb integrals for $K = 1s\alpha, 1s\beta, 2s\alpha, 2s\beta, 2p_z\alpha,$ and $2p_y\alpha$. but exchange contributions -only for $K = 1s\beta$ and $2s\beta$.

The UHF wave function can be used to describe bond breaking such as



However, the resulting energy curves can have slope jumps.



Slater-type orbitals (STOs)

$$\chi_{n,l,m}(r,\theta,\phi) = N_{n,l,m,\zeta} Y_{l,m}(\theta,\phi) r^{n-1} e^{-\zeta r}$$

are characterized by quantum numbers n , l , and m and exponents (which characterize the radial 'size') ζ .

Cartesian Gaussian-type orbitals (GTOs)

$$\chi_{a,b,c}(r,\theta,\phi) = N'_{a,b,c,\alpha} x^a y^b z^c \exp(-\alpha r^2),$$

are characterized by quantum numbers a , b , and c , which detail the angular shape and direction of the orbital, and exponents α which govern the radial 'size'.

Of course, for both functions, they are also characterized by where they are located (e.g., a nucleus or bond midpoint).

Slater-type orbitals are similar to Hydrogenic orbitals in the regions close to the nuclei. Specifically, they have a non-zero slope near the nucleus on which they are located (i.e., $d/dr(\exp(-\zeta r))_{r=0} = -\zeta$, so they can **have proper electron-nucleus cusps**.

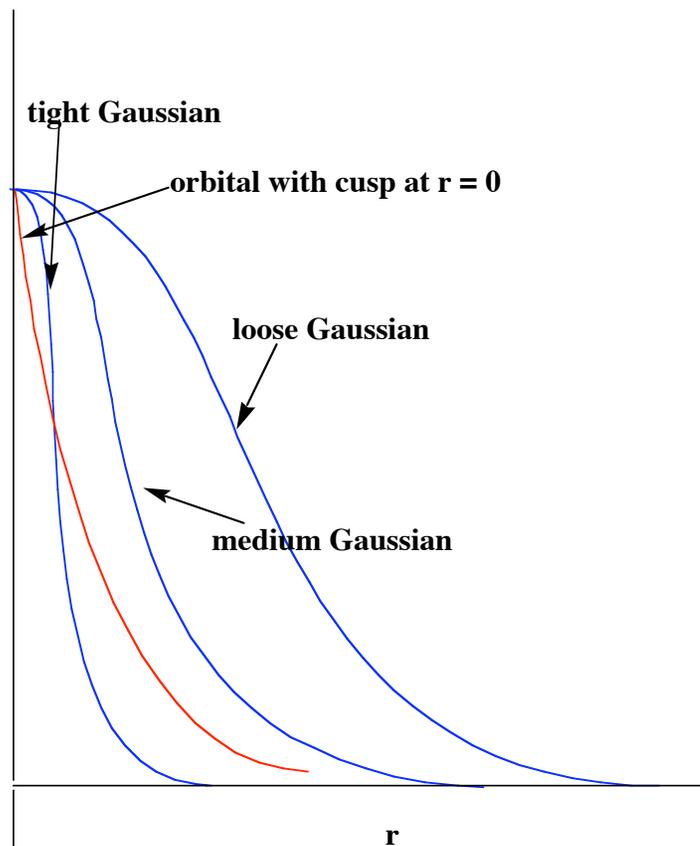
In contrast, **GTOs have zero slope near $r=0$** because

$$d/dr(\exp(-\alpha r^2))_{r=0} = 0.$$

This characteristic favors STOs over GTOs because we know that the correct solutions to the Schrödinger equation have such cusps at each nucleus of a molecule.

However, the **multi-center integrals** which arise in polyatomic-molecule calculations cannot efficiently be evaluated when STOs are employed. In contrast, such integrals can routinely be computed when GTOs are used. This advantage of GTOs has led to the dominance of these functions in molecular quantum chemistry.

To overcome the cusp weakness of GTO functions, it is common to combine two, three, or more GTOs, with combination coefficients that are fixed and not treated as LCAO parameters, into new functions called **contracted** GTOs or CGTOs. However, it is not possible to correctly produce a cusp by combining any number of Gaussian functions because every Gaussian has a zero slope at $r = 0$ as shown below.



Most AO basis sets contain a mixture of different classes of functions.

Fundamental **core and valence** basis functions

Polarization functions

Diffuse functions

Rydberg functions

Minimal basis-the number of CGTOs equals the number of core and valence atomic orbitals in the atom.

Carbon- one tight s-type CGTO, one looser s-type CGTO and a set of three looser p-type CGTOs.

Double-zeta (DZ)- twice as many CGTOs as there are core and valence atomic orbitals.

Carbon- two tight s, two looser s, and two sets of three looser p CGTOs.

The use of more basis functions is motivated by a desire to provide additional variational flexibility so the LCAO process can generate molecular orbitals of variable diffuseness as the local electronegativity of the atom varies.

Triple-zeta (TZ)- three times as many CGTOs as the number of core and valence atomic orbitals (extensions to quadruple-zeta and higher-zeta bases also exist).

Polarization functions- one higher angular momentum than appears in the atom's valence orbital space.

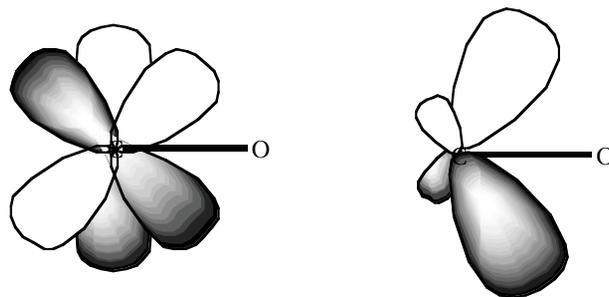
d-functions for C, N, and O and p-functions for H with exponents (ζ or α) which cause their radial sizes to be similar to the sizes of the valence orbitals.

Note- the **polarization p orbitals** of H are **similar in size** to the **valence 1s orbital** and the polarization d orbitals of C are similar in size to the 2s and 2p orbitals, not like the valence d orbitals of C.

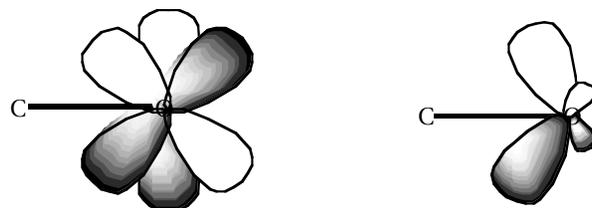
Polarization functions give angular flexibility to the LCAO process in forming molecular orbitals between from valence atomic orbitals.

Polarization functions also allow for angular correlations in describing the correlated motions of electrons.

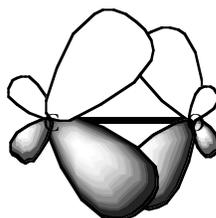
An example of d polarization functions on C and O



Carbon p_π and d_π orbitals combining to form a bent π orbital



Oxygen p_π and d_π orbitals combining to form a bent π orbital



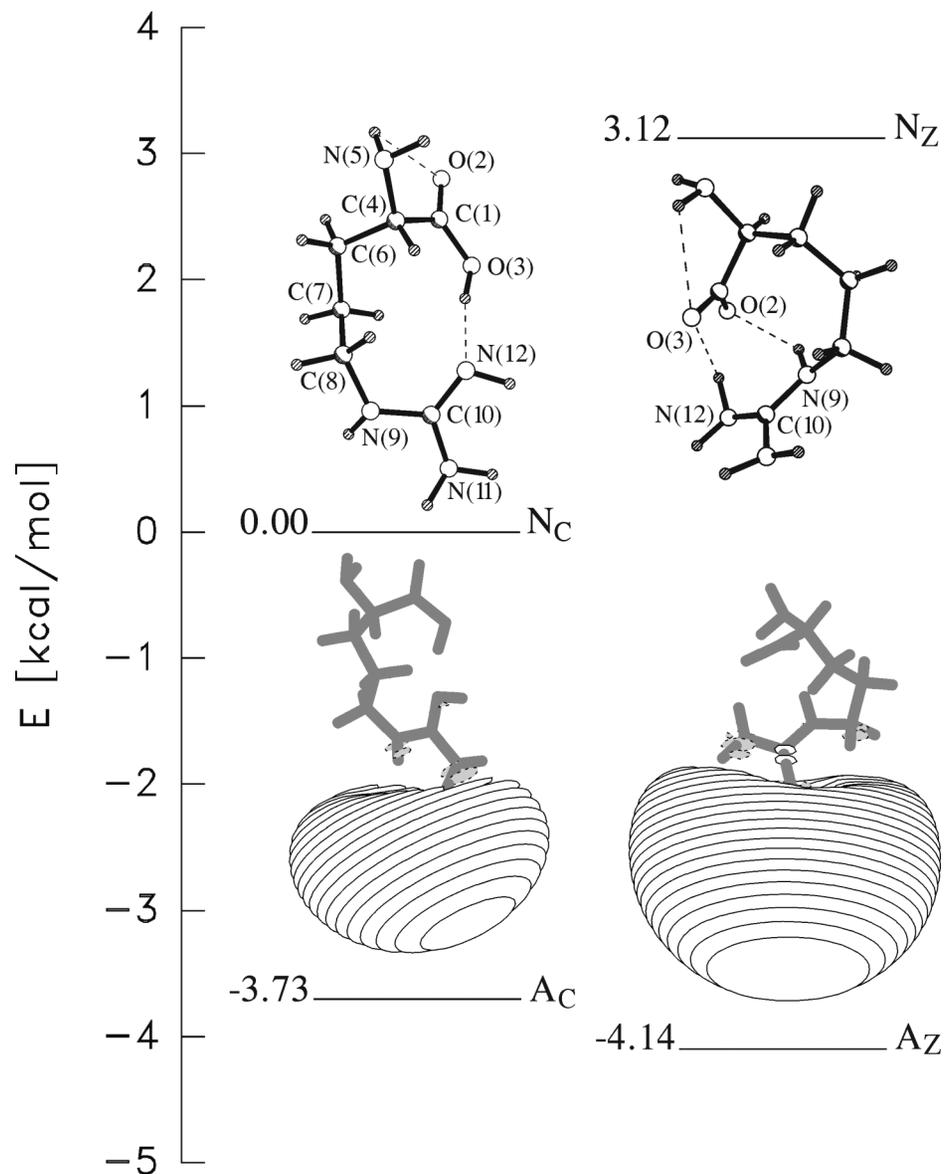
π bond formed from C and O bent (polarized) AOs

Valence and polarization functions do not provide enough radial flexibility to adequately describe very diffuse charge densities.

The **diffuse basis functions** tabulated on the PNNL web site are appropriate if the anion under study has its excess electron in a valence-type orbital (e.g., as in F^- , OH^- , carboxylates, etc.) but not for very weakly bound anions (e.g., having EAs of 0.1 eV or less).

For an electron in a **Rydberg** orbital, in an orbital centered on the positive site of a zwitterion species, or in a dipole-bound orbital, one must add to the bases containing valence, polarization, and conventional diffuse functions yet another set of functions that are extra diffuse. The exponents of these extra diffuse basis functions can be obtained by scaling the conventional diffuse functions' smallest exponent (e.g, by 1/3).

An example of a species needing extra diffuse basis functions- Arginine anion



aug-cc-pVTZ, cc-pVQZ, pVDZ.

VDZ, VTZ, VQZ or V5Z specifies at what level the valence (V) AOs are described. Nothing is said about the core orbitals because each of them is described by a single contracted Gaussian type basis orbital.

“**cc**” specifies that the orbital exponents and contraction coefficients were determined by requiring the atomic energies computed using a correlated method to agree to within some tolerance with experimental data. If cc is missing, the AO exponents and contraction coefficients were determined to make the Hartree-Fock atomic state energies agree with experiment to some precision.

“**p**” specifies that polarization basis orbitals have been included in the basis.

The number and kind of polarization functions differs depending on what level (i.e., VDZ through V5Z) the valence orbitals are treated.

For **C** at the VDZ level, one set of d polarization functions is added. At the VTZ, two sets of d and one set of f polarization functions are included. At the VQZ level, three d, two f, and one g set of polarization functions are present, and at the V5Z, four d, three f, two g and one h sets of polarization functions are included. This strategy of building bases has proven especially useful when carrying out complete-basis extrapolations.

“**aug**” specifies that (conventional) diffuse basis functions have been added, but the number and kind depend on how the valence basis is described. At the pVDZ level, one s, one p, and one d diffuse function appear; at pVTZ a diffuse f function also is present; at pVQZ a diffuse g set is also added; and at pV5Z a diffuse h set is present.

6-31+G or 3-21G*, 6-311+G*, or 6-31++G**

3- or 6- specifies that the core orbitals are described in terms of a single contracted Gaussian orbital having 3 or 6 terms.

-21 or -31 specifies that there are two valence basis functions of each type (i.e., the valence basis is of double-zeta quality), one being a contraction of 2 or 3 Gaussian orbitals and the other (the more diffuse of the two) being a contraction of a single Gaussian orbital.

-311 specifies that the valence orbitals are treated at the triple-zeta level with the tightest contracted function being a combination of 3 Gaussian orbitals and the two looser functions being a single Gaussian function.

* specifies that polarization functions have been included on the atoms other than hydrogen; ** specifies that polarization functions are included on all atoms, including the hydrogen atoms.

+ denotes that a single set of (conventional) diffuse valence basis AOs have been included; ++ means that two such sets of diffuse valence basis AOs are present.

Read the supplementary material to see if you understand that a Carbon Aug-cc-pV5Z basis has 127 contracted basis functions built from 209 primitive functions.

Keep in mind how things scale with the number of basis functions:

Calculating two-electron integrals $\langle \chi_a(1)\chi_b(2) | 1/r_{1,2} | \chi_c(1)\chi_d(2) \rangle$ - M^4

Solving the HF matrix eigenvalue equations for ϵ_k and φ_k - M^3

Now that AO bases have been discussed, let's return to discuss how one includes electron correlation in a calculation.

There are many ways and each has certain advantages and disadvantages.

Møller-Plesset perturbation (MPPT)- one uses the single-configuration (usually single determinant) SCF process to determine a set of spin-orbitals $\{\phi_i\}$. Then, using H^0 equal to the sum of the N electrons' Fock operators $H^0 = \sum_{i=1,N} F(i)$, perturbation theory is used to determine the C_I amplitudes for the CSFs. The amplitude for the reference CSF Φ is taken as unity and the other CSFs' amplitudes are determined by Rayleigh-Schrödinger perturbation using $H-H^0$ as the perturbation.

Advantages- Size extensive, no choices of “important” CSFs needed, decent scaling at low order (M^5 for MP2).

Disadvantages- Should not use if more than one determinant is “important” because it assumes the reference CSF is dominant.

MP2 energy and first-order wave function expressions:

$$\Psi^1 = - \sum_{i < j(\text{occ})} \sum_{m < n(\text{virt})} [\langle i, j | e^2/r_{1,2} | m, n \rangle - \langle i, j | e^2/r_{1,2} | n, m \rangle]$$

$$[\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j]^{-1} | \Phi_{i,j}^{m,n} \rangle$$

$$E = \langle \Phi | H^0 + V | \Phi + \Psi^1 \rangle = E_{\text{SCF}} - \sum_{i < j(\text{occ})} \sum_{m < n(\text{virt})}$$

$$| \langle i, j | e^2/r_{1,2} | m, n \rangle$$

$$- \langle i, j | e^2/r_{1,2} | n, m \rangle|^2 / [\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j].$$

Single excitations do not contribute to the first-order wave function (Brillouin theorem)

Two-electron integral transformation:

$\langle \phi_i \phi_j | e^2/r_{1,2} | \phi_k \phi_l \rangle$ is what you need

Use $\phi_j = \sum_{\mu} C_{j,\mu} \chi_{\mu}$ and begin with $\langle \chi_i \chi_j | e^2/r_{1,2} | \chi_k \chi_l \rangle$

to form

$$\langle \chi_i \chi_j | e^2/r_{1,2} | \chi_k \phi_m \rangle = \sum_l C_{m,l} \langle \chi_i \chi_j | e^2/r_{1,2} | \chi_k \chi_l \rangle. \quad M^5$$

and then

$$\langle \chi_i \chi_j | e^2/r_{1,2} | \phi_m \phi_m \rangle, \text{ and } \langle \chi_i \phi_j | e^2/r_{1,2} | \phi_k \phi_l \rangle,$$

and finally $\langle \phi_i \phi_j | e^2/r_{1,2} | \phi_k \phi_l \rangle$ $4M^5$ total operation.

Multiconfigurational self-consistent field (MCSCF)- the expectation value $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$, with Ψ being a combination of determinantal CSFs, is treated variationally and made stationary with respect to variations in both the C_I and the $C_{v,i}$ coefficients giving $\sum_J H_{I,J} C_J = E C_I$ and a set of HF-like equations for the $C_{v,I}$.

Advantages- can adequately describe bond cleavage, can give compact (in CSF-space) description of ψ , can be size extensive if CSF list is properly chosen, gives upper bound to energy.

Disadvantages- coupled orbital ($C_{i,\mu}$) and C_I optimization is a very large dimensional optimization with many local minima, so convergence is often a problem; unless the CSF list is large, not much dynamical correlation is included.

Configuration interaction (CI)- the LCAO-MO coefficients of all the spin-orbitals are determined first via a single-configuration SCF calculation or an MCSCF calculation using a small number of CSFs. The C_I coefficients are subsequently determined by making stationary the energy expectation value $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ which gives $\sum_J H_{I,J} C_J = E C_I$.

Advantages- Energies give upper bounds and are variational (so lower is better), one can obtain excited states from the CI matrix eigenvalue problem.

Disadvantages- Must choose “important” CSFs, not size extensive, scaling grows rapidly as the level of “excitations” in CSFs increases (M^5 for integral transformation; N_C^2 per electronic state).

Coupled-Cluster Theory (CC)- one expresses the wave function as

$$\Psi = \exp(T) \Phi,$$

where Φ is a single CSF (usually a single determinant) used in the SCF process to generate a set of spin-orbitals. The operator T is given in terms of operators that generate spin-orbital excitations

$$T = \sum_{i,m} t_i^m m^+ i + \sum_{i,j,m,n} t_{i,j}^{m,n} m^+ n^+ j i + \dots,$$

Here $m^+ i$ denotes creation of an electron in spin-orbital ϕ_m and removal of an electron from spin-orbital ϕ_i to generate a single excitation. The operation $m^+ n^+ j i$ represents a double excitation from $\phi_i \phi_j$ to $\phi_m \phi_n$.

When including in T only double excitations $\{ m^+ n^+ j i \}$, the CC wave function $\exp(T) \Phi$ contains contributions from double, quadruple, sextuple, etc. excited determinants:

$$\begin{aligned} \exp(T) \Phi = & \{ 1 + \sum_{m,n,Iij} t_{m,n,i,j} m^+ n^+ j i + 1/2 (\sum_{m,n,Iij} t_{m,n,i,j} m^+ n^+ j i) \\ & (\sum_{m,n,Iij} t_{m,n,i,j} m^+ n^+ j i) \\ & + 1/6 (\sum_{m,n,Iij} t_{m,n,i,j} m^+ n^+ j i) (\sum_{m,n,Iij} t_{m,n,i,j} m^+ n^+ j i) \\ & (\sum_{m,n,Iij} t_{m,n,i,j} m^+ n^+ j i) + \dots \} \Phi. \end{aligned}$$

But note that the amplitudes of the higher excitations are given as products of amplitudes of lower excitations (unlinked).

To obtain the equations of CC theory, one writes

$$H \exp(T) \Phi = E \exp(T) \Phi, \text{ then}$$

$$\exp(-T) H \exp(T) \Phi = E \Phi, \text{ then}$$

uses the Baker-Campbell-Hausdorff expansion

$$\exp(-T) H \exp(T) = H - [T, H] + 1/2 [[T, T, H]] - 1/6 [[[T, T, T, T, H]]] + \dots$$

The equations one must solve for the t amplitudes are quartic:

$$\langle \Phi_i^m | H + [H, T] + 1/2 [[H, T], T] + 1/6 [[[H, T], T], T] + 1/24 [[[[H, T], T], T], T] | \Phi \rangle = 0;$$

$$\langle \Phi_{i,j}^{m,n} | H + [H, T] + 1/2 [[H, T], T] + 1/6 [[[H, T], T], T] + 1/24 [[[[H, T], T], T], T] | \Phi \rangle = 0;$$

$$\langle \Phi_{i,j,k}^{m,n,p} | H + [H, T] + 1/2 [[H, T], T] + 1/6 [[[H, T], T], T] + 1/24 [[[[H, T], T], T], T] | \Phi \rangle = 0,$$

The amplitudes of the double excitations that arise in the lowest approximation are identical to those of MP2

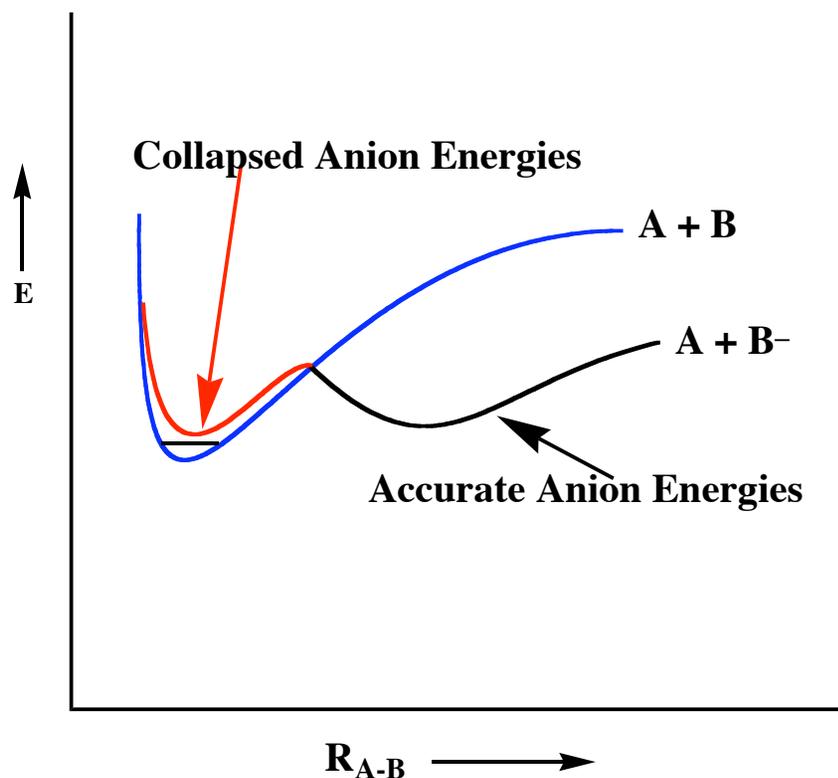
$$t_{i,j}^{m,n} = - \langle i,j | e^2/r_{1,2} | m,n \rangle / [\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j].$$

Summary

1. **Basis sets** should be used that (i) are flexible in the valence region to allow for the different radial extents of the neutral and anion's orbitals, (ii) include polarization functions to allow for good treatment of electron correlations, and (iii) include extra diffuse functions if very weak electron binding is anticipated. For high precision, it is useful to carry out basis set extrapolations using results calculated with a range of basis sets (e.g., VDZ, VTZ, VQZ).
2. **Electron correlation** should be included because correlation energies are significant (e.g., 0.5 eV per electron pair). Correlation allows the electrons to avoid one another by forming polarized orbital pairs. There are many ways to handle electron correlation (e.g., CI, MPn, CC, DFT, MCSCF).
3. **Single determinant** zeroth order wave functions may not be adequate if the spin and space symmetry adapted wave function requires more than one determinant. Open-shell singlet wave functions are the most common examples for which a single determinant can not be employed. In such cases, methods that assume dominance of a single determinant should be avoided.
4. The **computational cost** involved in various electronic structure calculations scales in a highly non-linear fashion with the size of the AO basis, so careful basis set choices must be made.

Special Tricks for calculating an anion's energy when it lies above that of the neutral?

Straightforward variational calculations will “collapse”
To produce a wave function and energy appropriate to
The neutral molecule plus a free electron with low energy.

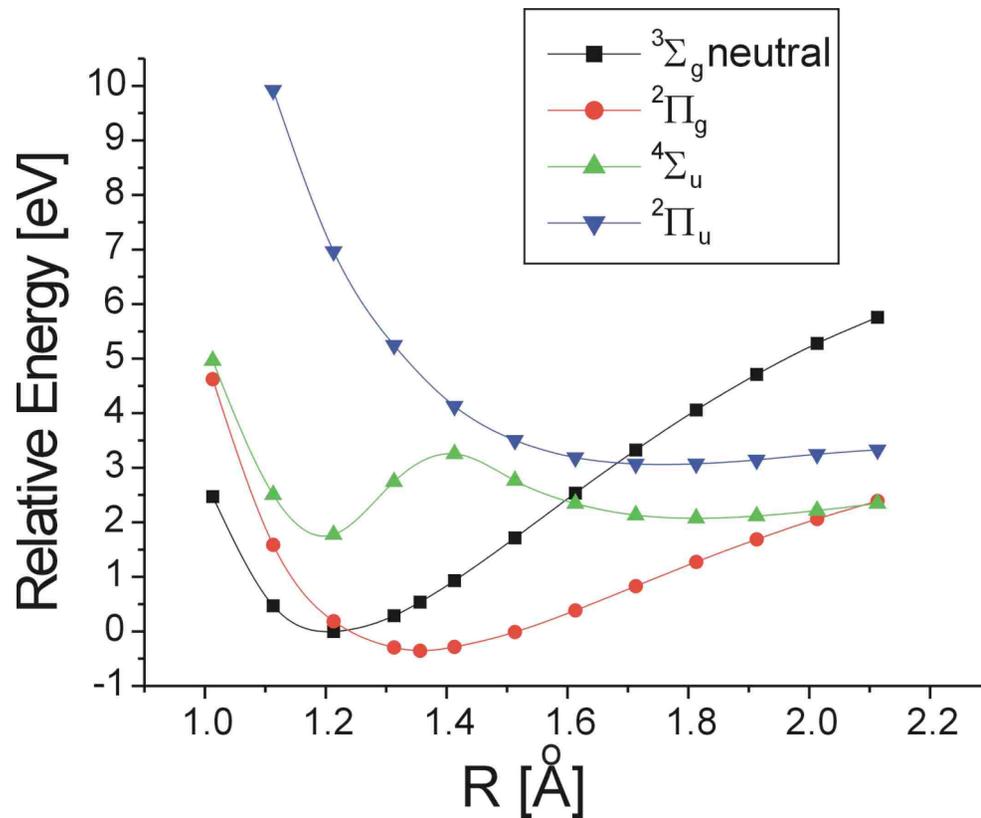


In the **charge-scaling** method, one fractionally increases the nuclear charges on the atoms involved in the bond, computes the anion-neutral energy difference as a function of δq , and extrapolates to $\delta q \rightarrow 0$.

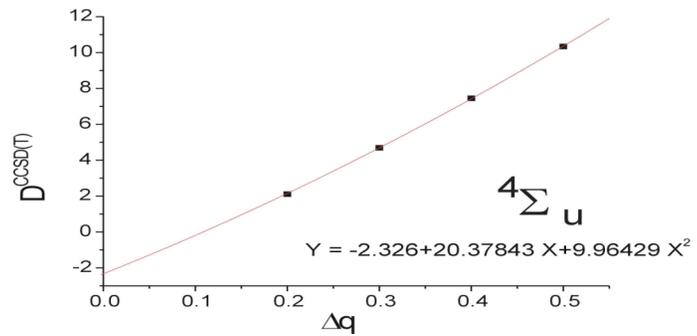
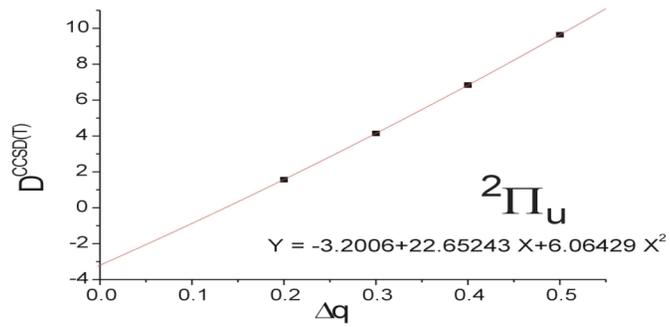
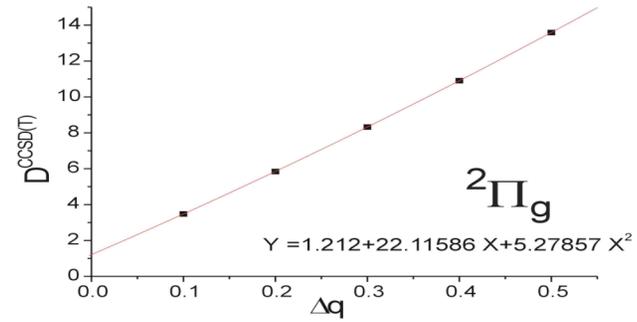
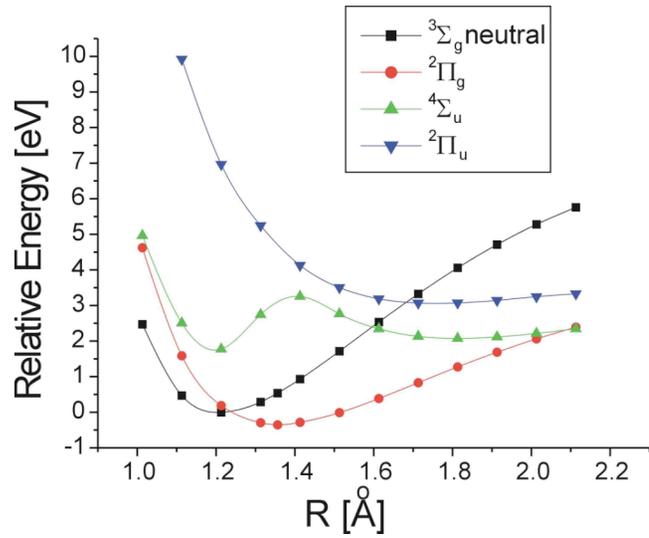
This is essential to do for species such as SO_4^{2-} or CO_3^{2-} , which are not stable as isolated species.

It is also essential when studying σ^* -attached states in, for example, $\text{Cl}_3\text{C-F} + e^- \rightarrow \text{Cl}_3\text{C} + \text{F}^-$ dissociative electron attachment or when attaching an electron to a σ^* orbital of benzene.

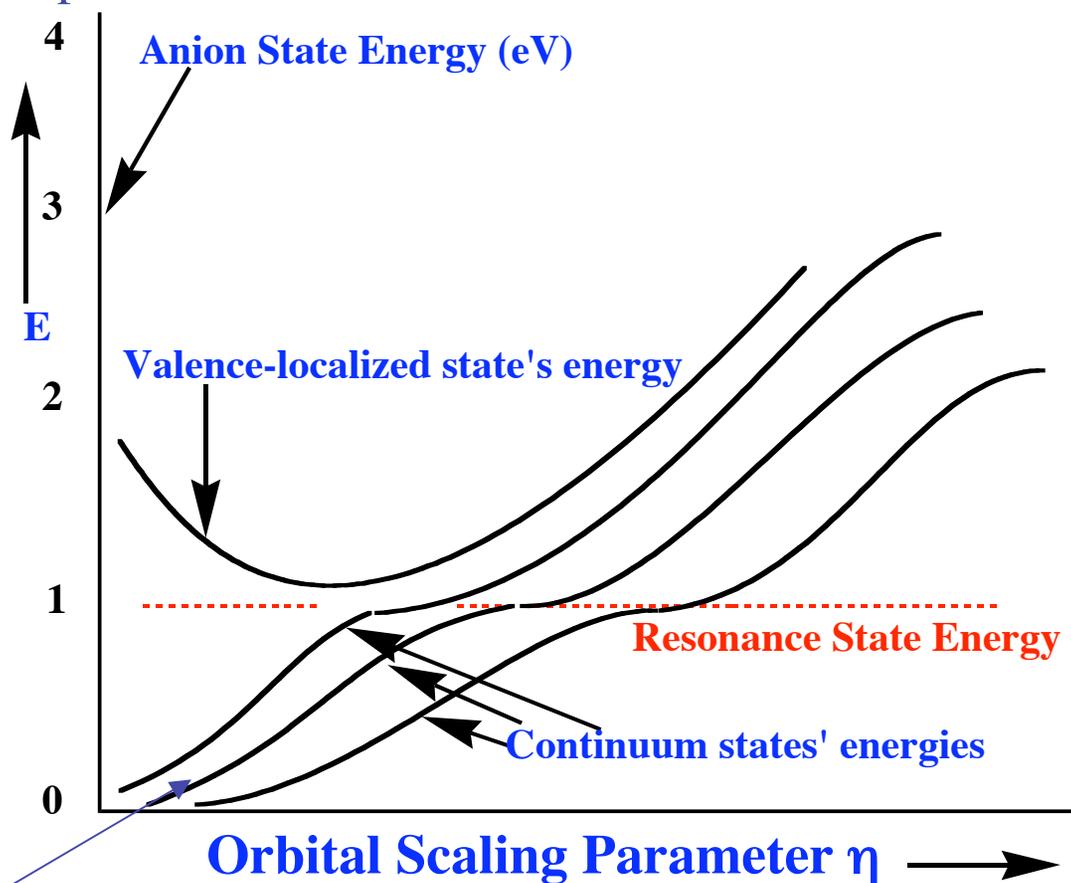
Consider calculating the Born-Oppenheimer energies of various states of O_2^- . All three lowest states have bond lengths where the anion is electronically unstable.



R=1.413 Å



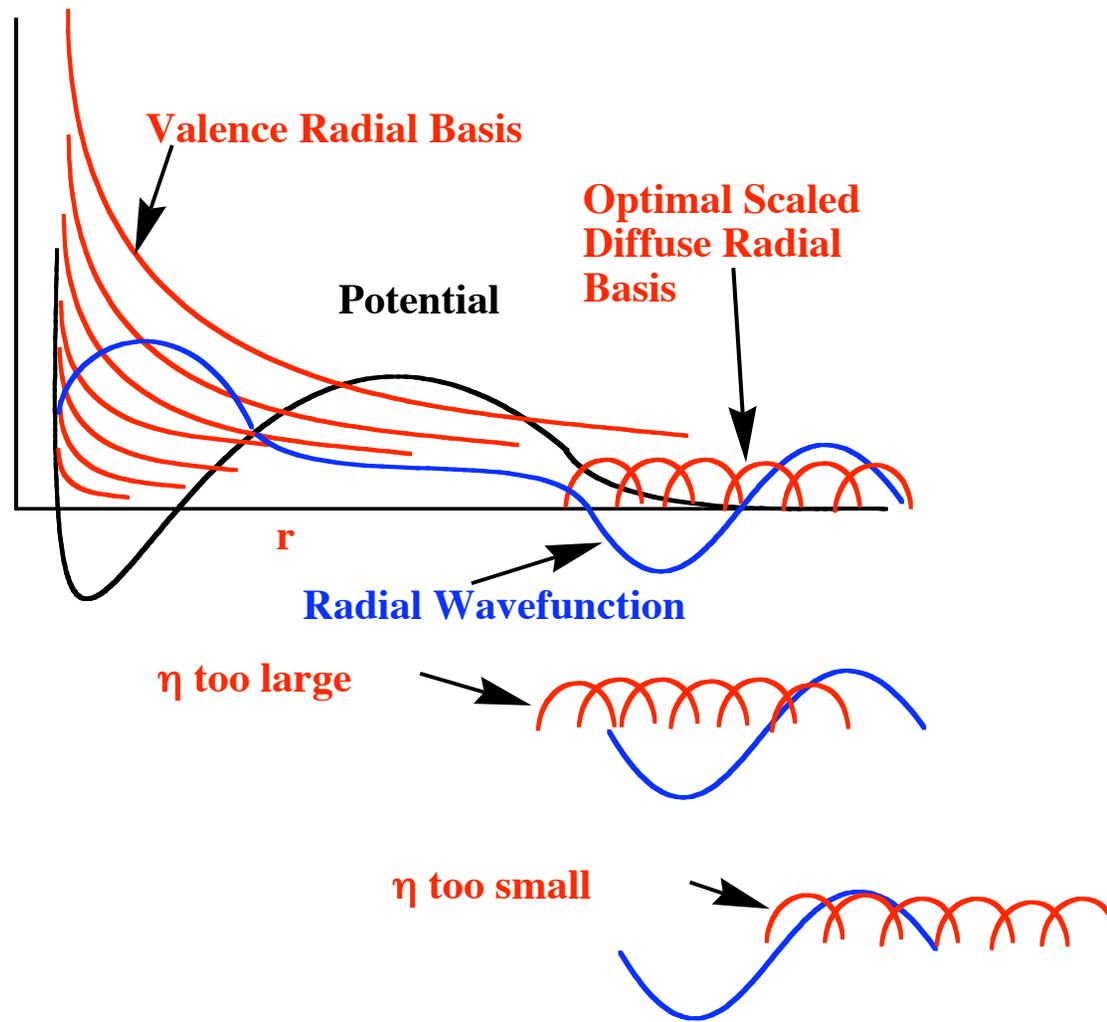
In the **stabilization method** one computes the anion-neutral energy difference in a series of basis sets whose more diffuse basis functions' exponents α are scaled $\alpha \rightarrow \eta \alpha$. Plotting the anion-neutral energy differences vs η produces a stabilization plot that can be used to determine the metastable state's energy.



These energies grow with η because T scales as η^2 .

This method requires one to compute the energies of many anion states.

At certain η values, the diffuse basis functions can be combined to describe the de Broglie λ of the asymptotic ψ and can match ψ and $d\psi/dr$ throughout.



The lower-energy curves describe the dominantly-continuum solutions' variation with η . When one of these solutions gains the proper de Broglie and can match the energy of the valence-localized state, an avoided crossing occurs. The energy of this crossing is the resonance energy.

