Non-Born Oppenheimer Contributions

Adiabatic Approximation 1

Include diagonal coupling term C_{nn}

(assuming the electron wavefunction is REAL)

$$C_{nn} = \left\langle n \middle| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 \middle| n \right\rangle + \left\langle n \middle| -\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I \middle| n \right\rangle \nabla_I$$

$$\langle n \| n \rangle = 1 \rightarrow \nabla_I \langle n \| n \rangle = \nabla_I \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= \int \nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} + \int \phi_n^{el}(\mathbf{r};\mathbf{R})\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= 2\left[\int \phi_n^{el}(\mathbf{r};\mathbf{R})\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}\right] = 2\left[\int \nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}\right] = 0$$

so

$$\int \phi_n^{el}(\mathbf{r};\mathbf{R})\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} = \int \nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} = 0$$

Adiabatic Approximation 2

Include diagonal coupling term C_{nn}

Second term is zero

$$C_{nn} = \left\langle n \middle| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 \middle| n \right\rangle + \left\langle n \middle| -\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I \middle| n \right\rangle \nabla_I$$

$$\nabla_I^2 \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= \nabla_I \int \nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} + \nabla_I \int \phi_n^{el}(\mathbf{r};\mathbf{R})\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= \nabla_I 2\int \phi_n^{el}(\mathbf{r};\mathbf{R})\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= 2\int \phi_n^{el}(\mathbf{r};\mathbf{R})\nabla_I^2 \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} + 2\int \left|\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\right|^2 d\mathbf{r} = 0$$

$$\int \phi_n^{el}(\mathbf{r};\mathbf{R})\nabla_I^2 \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} = -\int \left|\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\right|^2 d\mathbf{r}$$

$$C_{nn} = \left\langle n \middle| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 \middle| n \right\rangle = \frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\int \left|\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\right|^2 d\mathbf{r}$$

Non-adiabatic Matrix Elements when is it important?

$$\sum_{m}^{\infty}\left\langle n\left|-\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\right|m\right\rangle \nabla_I\chi_m(\mathbf{R})$$

Assuming 1 dimension X coordinate of atom I

$$\left(\frac{\partial}{\partial X_I}\hat{H}^0-\hat{H}^0\frac{\partial}{\partial X_I}\right)\left|m\right\rangle=\left(\hat{H}^0\frac{\partial}{\partial X_I}+\frac{\partial\hat{H}^0}{\partial X_I}-\hat{H}^0\frac{\partial}{\partial X_I}\right)\left|m\right\rangle=\frac{\partial\hat{H}^0}{\partial X_I}\left|m\right\rangle$$

$$\left\langle n\left|\frac{\partial}{\partial X_I}\hat{H}^0-\hat{H}^0\frac{\partial}{\partial X_I}\right|m\right\rangle=\left(E_m(X_I)-E_n(X_I)\right)\left\langle n\left|\frac{\partial}{\partial X_I}\right|m\right\rangle=\left\langle n\left|\frac{\partial\hat{H}^0}{\partial X_I}\right|m\right\rangle$$

$$\left\langle n\left|\frac{\partial}{\partial X_I}\right|m\right\rangle=\frac{\left\langle n\left|\frac{\partial\hat{H}^0}{\partial X_I}\right|m\right\rangle}{\left(E_m(X_I)-E_n(X_I)\right)}$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})=-\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2+\left[\sum_{I=1}^{N}\sum_{J\neq I}^{N}\frac{Z_IZ_J}{\left|\mathbf{R}_I-\mathbf{R}_J\right|}-\sum_{I=1}^{N}\sum_{i=1}^{n}\frac{Z_I}{\left|\mathbf{R}_I-\mathbf{r}_i\right|}+\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}\right]$$

Non-adiabatic Matrix Element

$$\left\langle n \middle| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 \middle| m \right\rangle$$

Assuming 1 dimension X coordinate of atom I
Electonic wavefunction is a real function

$$\frac{\partial}{\partial X_I}\left\langle n \middle| \frac{\partial}{\partial X_I} \middle| m \right\rangle = \left\langle \frac{\partial}{\partial X_I} n \middle| \frac{\partial}{\partial X_I} \middle| m \right\rangle + \left\langle n \middle| \frac{\partial^2}{\partial X_I^2} \middle| m \right\rangle$$

$$= \sum_{l}^{\infty}\left\langle \frac{\partial}{\partial X_I} n \middle| l \right\rangle \left\langle l \middle| \frac{\partial}{\partial X_I} m \right\rangle + \left\langle n \middle| \frac{\partial^2}{\partial X_I^2} \middle| m \right\rangle$$

Assuming real electron wavefunction

$$\left\langle n \middle| \frac{\partial^2}{\partial X_I^2} \middle| m \right\rangle = \frac{\partial}{\partial X_I}\left\langle n \middle| \frac{\partial}{\partial X_I} \middle| m \right\rangle - \sum_{l}^{\infty}\left\langle l \middle| \frac{\partial}{\partial X_I} \middle| n \right\rangle \left\langle l \middle| \frac{\partial}{\partial X_I} \middle| m \right\rangle$$

Second derivative term for the non-adiabatic matrix element is **derivative of the first matrix derivative and product of two first derivative matrix,** so if first derivative matrix is small these terms will also be small

Non-adiabatic Matrix Element

$$\sum_{m}^{\infty} C_{nm}\chi_m(\mathbf{R})$$

$$\equiv \sum_{m}^{\infty}\left\langle n\left|-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right|m\right\rangle\chi_m(\mathbf{R})+\sum_{m}^{\infty}\left\langle n\left|-\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\right|m\right\rangle\nabla_I\chi_m(\mathbf{R})$$

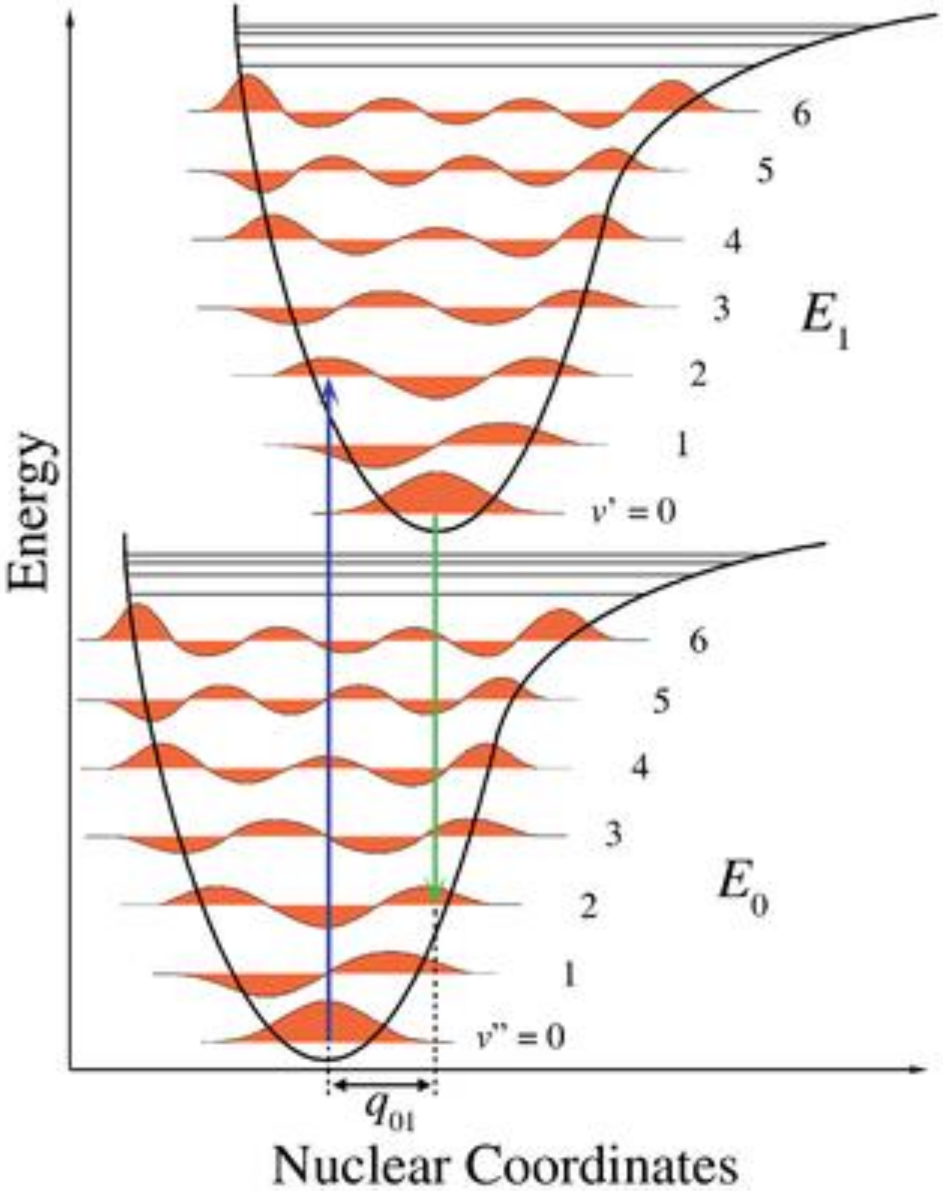
$$\left\langle n\left|-\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\right|m\right\rangle=\sum_{I=1}^{N}-\frac{1}{M_I}\frac{\left\langle n\left|\nabla_I H^0\right|m\right\rangle}{E_m(\mathbf{R})-E_n(\mathbf{R})}$$

$$\left\langle n\left|-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right|m\right\rangle=-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\left\langle n\left|\nabla_I\right|m\right\rangle$$

$$+\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\sum_{l=1}^{N}\left\langle l\left|\nabla_I\right|n\right\rangle\left\langle l\left|\nabla_I\right|m\right\rangle$$

Normal Potential Surface

BO is good



This is when BO is good?

How much is error from BO approximation?

Present State of Art Gas Phase Water results: using time

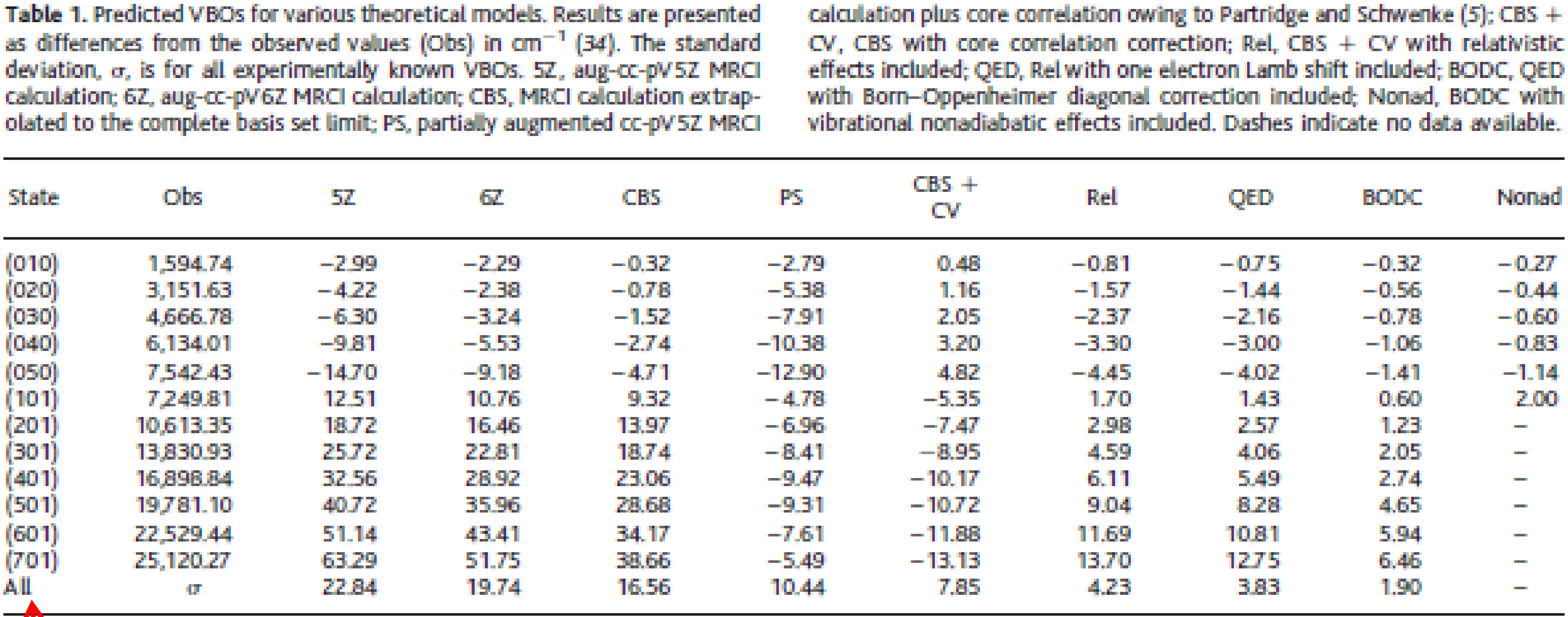
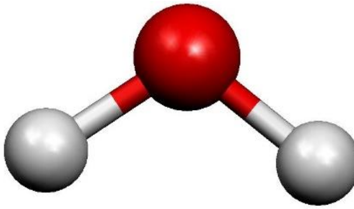


Table 1. Predicted VBOs for various theoretical models. Results are presented as differences from the observed values (Obs) in cm^{-1} (34). The standard deviation, σ, is for all experimentally known VBOs. 5Z, aug-cc-pV5Z MRCI calculation; 6Z, aug-cc-pV6Z MRCI calculation; CBS, MRCI calculation extrapolated to the complete basis set limit; PS, partially augmented cc-pV5Z MRCI calculation plus core correlation owing to Partridge and Schwenke (5); CBS + CV, CBS with core correlation correction; Rel, CBS + CV with relativistic effects included; QED, Rel with one electron Lamb shift included; BODC, QED with Born–Oppenheimer diagonal correction included; Nonad, BODC with vibrational nonadiabatic effects included. Dashes indicate no data available.

State	Obs	5Z	6Z	CBS	PS	CBS + CV	Rel	QED	BODC	Nonad
(010)	1,594.74	−2.99	−2.29	−0.32	−2.79	0.48	−0.81	−0.75	−0.32	−0.27
(020)	3,151.63	−4.22	−2.38	−0.78	−5.38	1.16	−1.57	−1.44	−0.56	−0.44
(030)	4,666.78	−6.30	−3.24	−1.52	−7.91	2.05	−2.37	−2.16	−0.78	−0.60
(040)	6,134.01	−9.81	−5.53	−2.74	−10.38	3.20	−3.30	−3.00	−1.06	−0.83
(050)	7,542.43	−14.70	−9.18	−4.71	−12.90	4.82	−4.45	−4.02	−1.41	−1.14
(101)	7,249.81	12.51	10.76	9.32	−4.78	−5.35	1.70	1.43	0.60	2.00
(201)	10,613.35	18.72	16.46	13.97	−6.96	−7.47	2.98	2.57	1.23	–
(301)	13,830.93	25.72	22.81	18.74	−8.41	−8.95	4.59	4.06	2.05	–
(401)	16,898.84	32.56	28.92	23.06	−9.47	−10.17	6.11	5.49	2.74	–
(501)	19,781.10	40.72	35.96	28.68	−9.31	−10.72	9.04	8.28	4.65	–
(601)	22,529.44	51.14	43.41	34.17	−7.61	−11.88	11.69	10.81	5.94	–
(701)	25,120.27	63.29	51.75	38.66	−5.49	−13.13	13.70	12.75	6.46	–
All	σ	22.84	19.74	16.56	10.44	7.85	4.23	3.83	1.90	–



Complete basis set gets you to 15 cm^{-1} accuracy

Addition of core valence gets you to 8 cm^{-1}

Relativistic lowers 4 cm^{-1}, QED does not change much

and addition of nonBO gets you to 2 cm^{-1}

Include transitions to 30,000cm^{-1} O L Polyansky et al. Science 299, 539 (

Non-adiabatic Matrix Element

$$\sum_m^\infty C_{nm}\chi_m(\mathbf{R})$$

$$\equiv \sum_m^\infty \left\langle n \left| -\frac{1}{2}\sum_{I=1}^N \frac{1}{M_I}\nabla_I^2 \right| m \right\rangle \chi_m(\mathbf{R}) + \sum_m^\infty \left\langle n \left| -\sum_{I=1}^N \frac{1}{M_I}\nabla_I \right| m \right\rangle \nabla_I \chi_m(\mathbf{R})$$

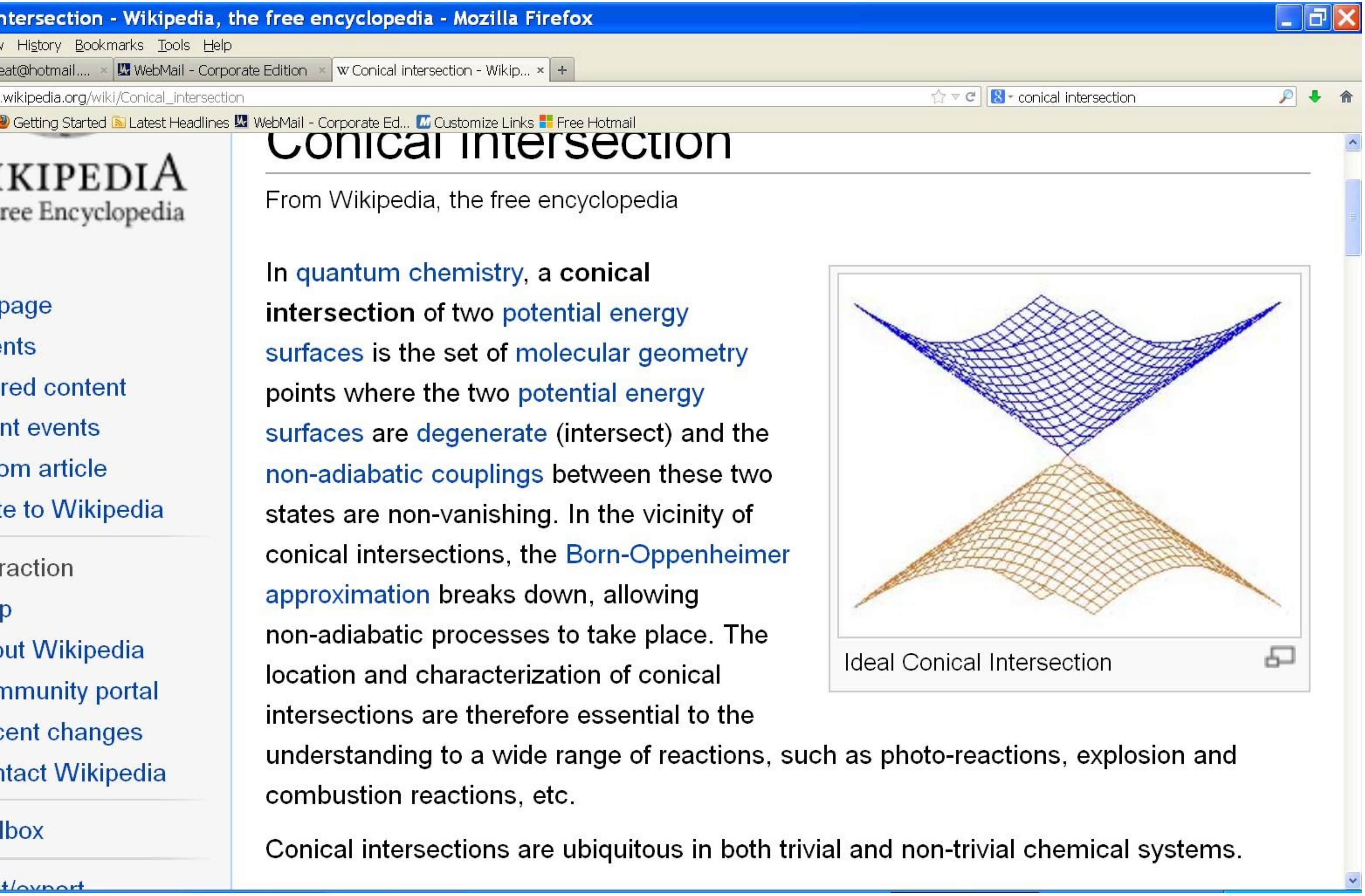
$$\left\langle n \left| -\sum_{I=1}^N \frac{1}{M_I}\nabla_I \right| m \right\rangle = \sum_{I=1}^N -\frac{1}{M_I}\frac{\langle n|\nabla_I H^0|m\rangle}{E_m(\mathbf{R})-E_n(\mathbf{R})}$$

What happens if nergies of two electronic states are close to each other!

$$E_m(\boldsymbol{R}) - E_n(\boldsymbol{R}) \to 0$$

$$\left\langle n \left| -\frac{1}{2}\sum_{I=1}^N \frac{1}{M_I}\nabla_I^2 \right| m \right\rangle = -\frac{1}{2}\sum_{I=1}^N \frac{1}{M_I}\nabla_I \langle n|\nabla_I|m\rangle$$

$$+\frac{1}{2}\sum_{I=1}^N \frac{1}{M_I}\sum_{l=1}^N \langle l|\nabla_I|n\rangle\langle l|\nabla_I|m\rangle$$



Conical intersection

From Wikipedia, the free encyclopedia

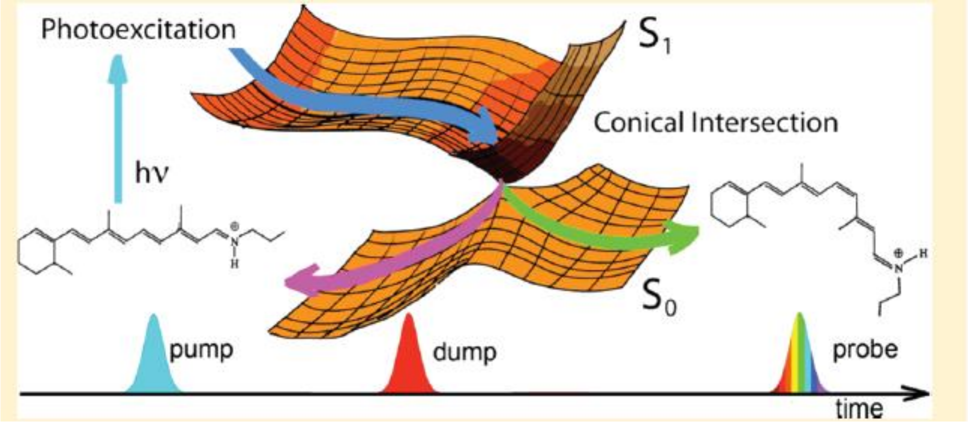
In quantum chemistry, a **conical intersection** of two potential energy surfaces is the set of molecular geometry points where the two potential energy surfaces are degenerate (intersect) and the non-adiabatic couplings between these two states are non-vanishing. In the vicinity of conical intersections, the Born-Oppenheimer approximation breaks down, allowing non-adiabatic processes to take place. The location and characterization of conical intersections are therefore essential to the understanding to a wide range of reactions, such as photo-reactions, explosion and combustion reactions, etc.

Ideal Conical Intersection

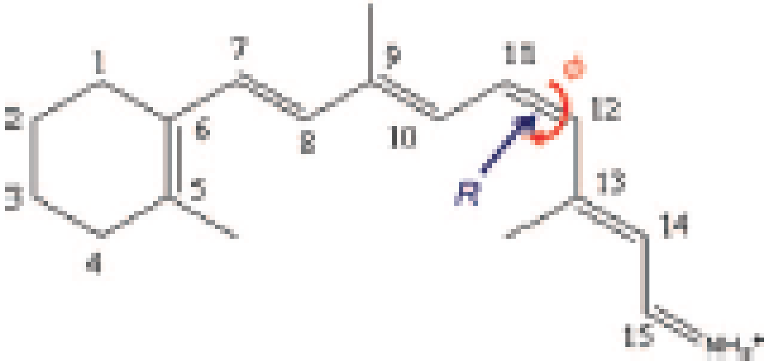
Conical intersections are ubiquitous in both trivial and non-trivial chemical systems.

Nonadiabatic Effects curve crossing

Retinal Chromophore Population Branching at Conical Intersection



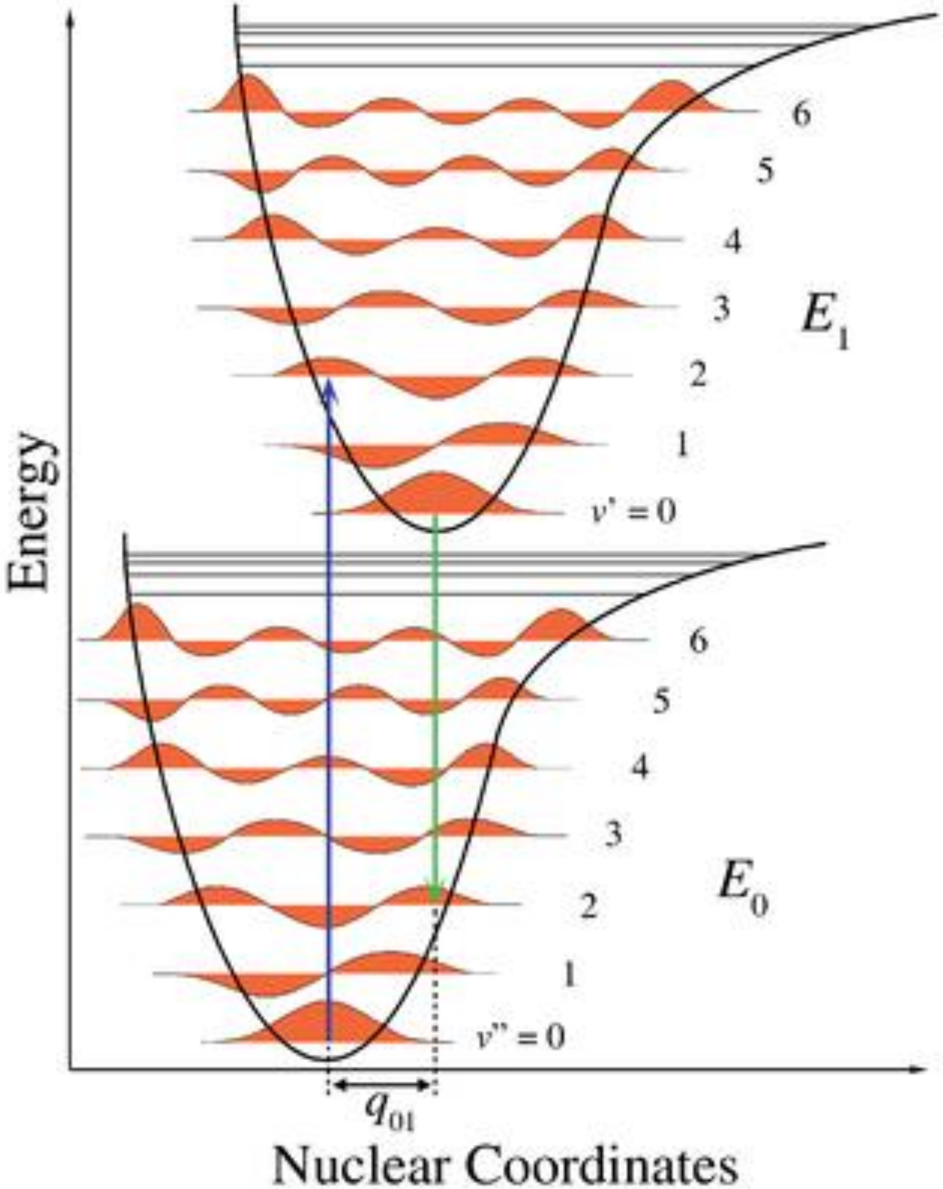
Parmigiani et al.
JACS, 134, 955 (2011).



T Ishida et al. JPC A 113, 4356 (

Normal Potential Surface

BO is good

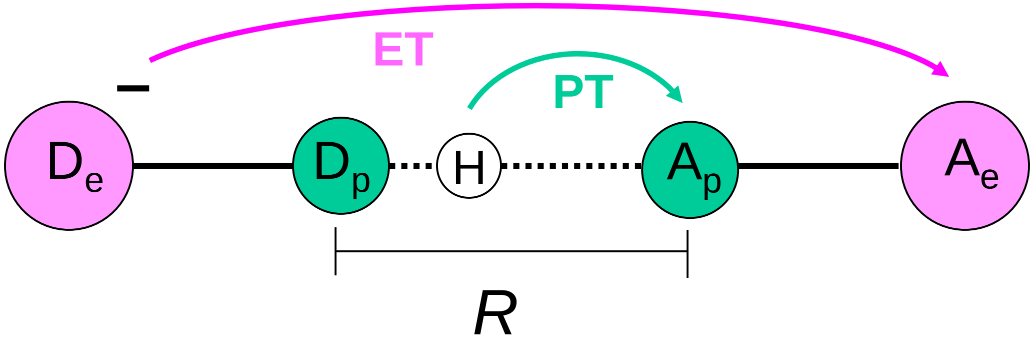


When will BO not be good?

Steal FROM Sharon Hammes-Schiffer's web page
http://www.scs.illinois.edu/schiffer/

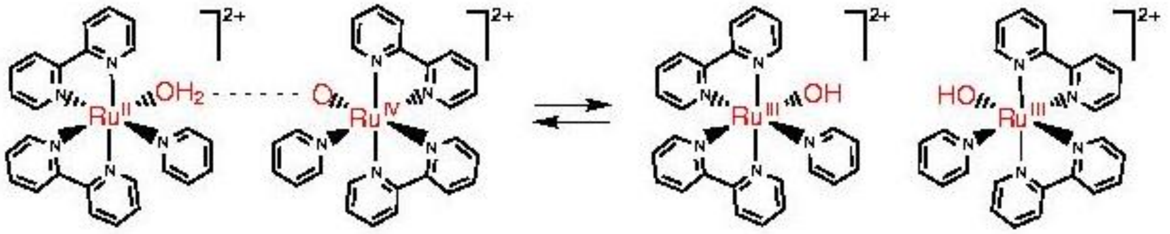
Theory of Proton-Coupled Electron Transfer

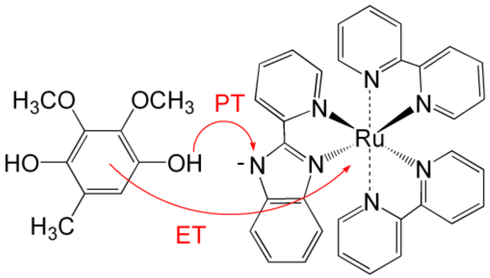
Sharon Hammes-Schiffer
Pennsylvania State University

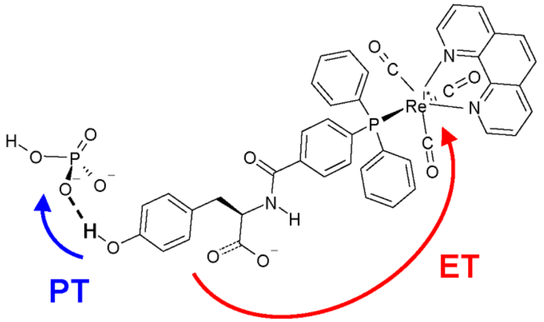


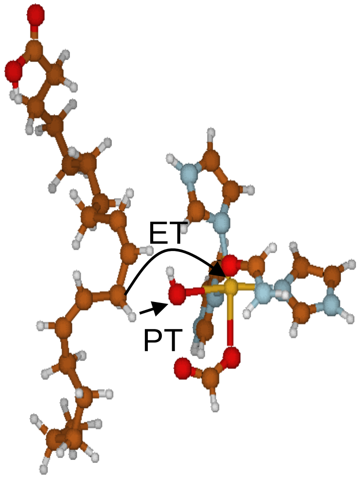
Note: Much of this information, along with more details, additional rate constant expressions, and full references to the original papers, is available in the following JPC Feature Article:
Hammes-Schiffer and Soudackov, JPC B **112**, 14108 (2008)

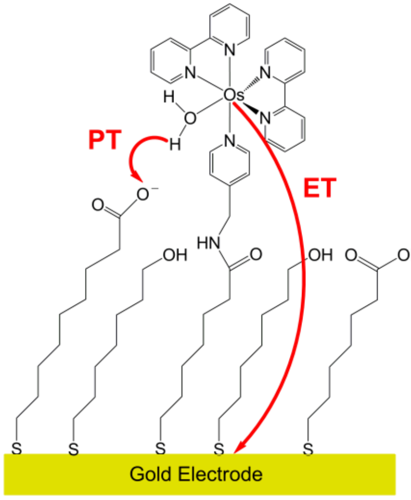
Examples of Concerted PCET





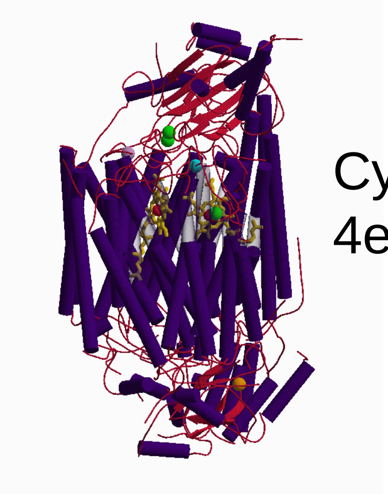






Importance of PCET

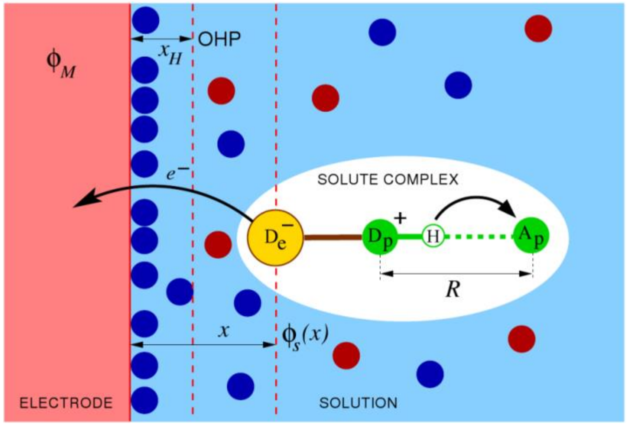
- Biological processes
  - photosynthesis
  - respiration
  - enzyme reactions
  - DNA



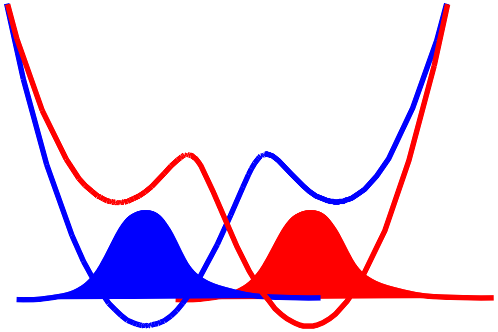
Cytochrome c oxidase

$4e^- + 4H^+ + O_2 \rightarrow 2(H_2O)$

- Electrochemical processes
  - fuel cells
  - solar cells
  - energy devices



Electron-Proton Vibronic States



H treated quantum mechanically

Calculate proton vibrational states
for electronic states I and II

- electronic states: $\Psi_{\mathrm{I}}(\mathbf{r}_e,\mathbf{r}_p)$, $\Psi_{\mathrm{II}}(\mathbf{r}_e,\mathbf{r}_p)$
- proton vibrational states: $\varphi_{\mathrm{I}\mu}(\mathbf{r}_p)$, $\varphi_{\mathrm{II}\nu}(\mathbf{r}_p)$

Reactant vibronic states: $\Phi^{\mathrm{I}}(\mathbf{r}_e,\mathbf{r}_p) = \Psi_{\mathrm{I}}(\mathbf{r}_e,\mathbf{r}_p)\,\varphi_{\mathrm{I}\mu}(\mathbf{r}_p)$
Product vibronic states: $\Phi^{\mathrm{II}}(\mathbf{r}_e,\mathbf{r}_p) = \Psi_{\mathrm{II}}(\mathbf{r}_e,\mathbf{r}_p)\,\varphi_{\mathrm{II}\nu}(\mathbf{r}_p)$

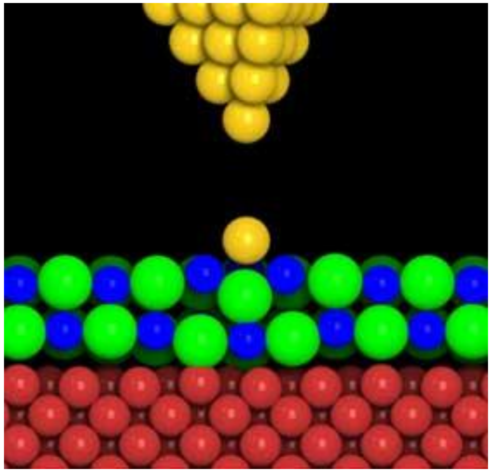
Coupling between reactant and product vibronic states typically much smaller than thermal energy because of small overlap → Describe reactions in terms of nonadiabatic transitions between reactant and product vibronic states

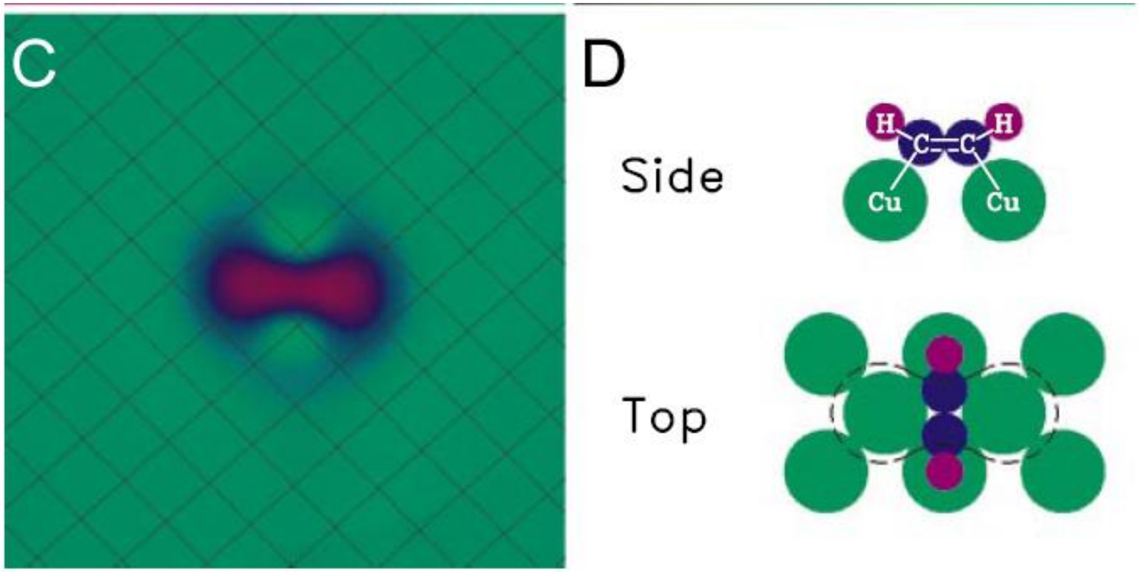
Vibronic states depend parametrically on other nuclear coords

Examples of Nonadiabatic effects

Molecular Vibrational Microscopy

HCCH on Cu surface

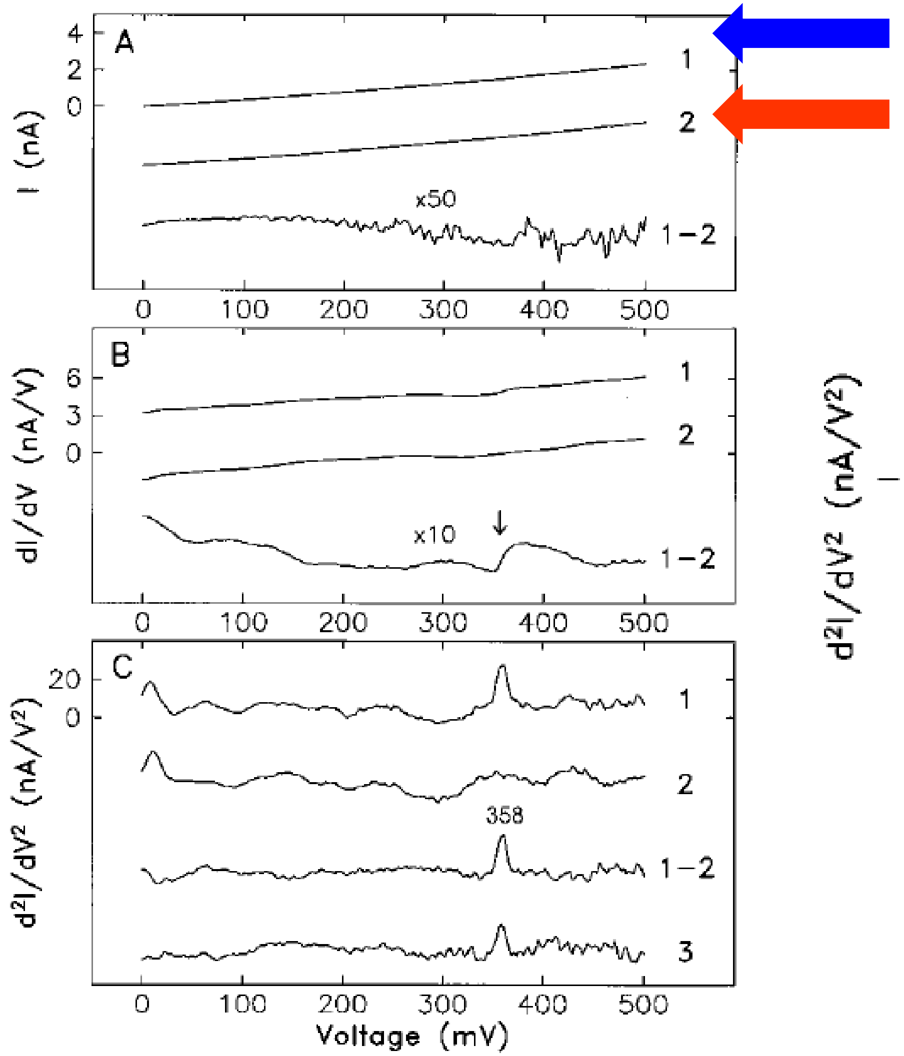




M Persson, PRL, 85, 2997-; W. Ho, Sicence 280 1732-

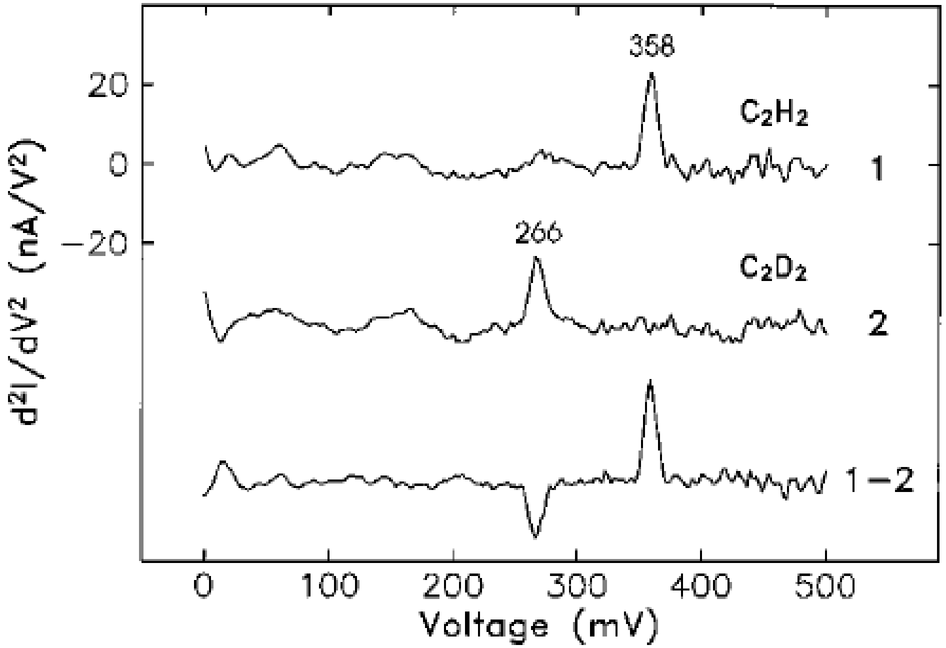
Molecular Vibrational Microscopy 2

Current as function of voltage



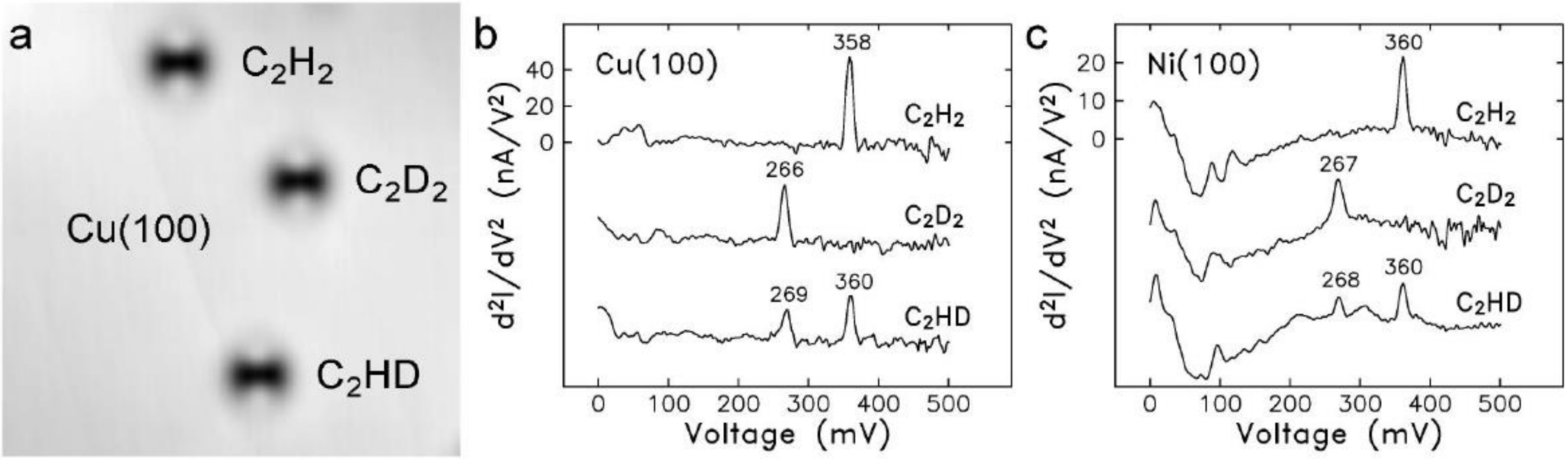
Clean Cu surface

HCCH on Cu surface



Putting on HCCH and DCCD

What about HCCD



358 meV=2887 cm^{-1}
266 meV=2145 cm^{-1}
$2887/2145=1.35\sim\sqrt{2}$

Electron motion is exciting vibrational motion of nuclei

W Ho PRL 82, 1724-

LCAO Approximation for Diatomic Molecules

Kaito Takahashi

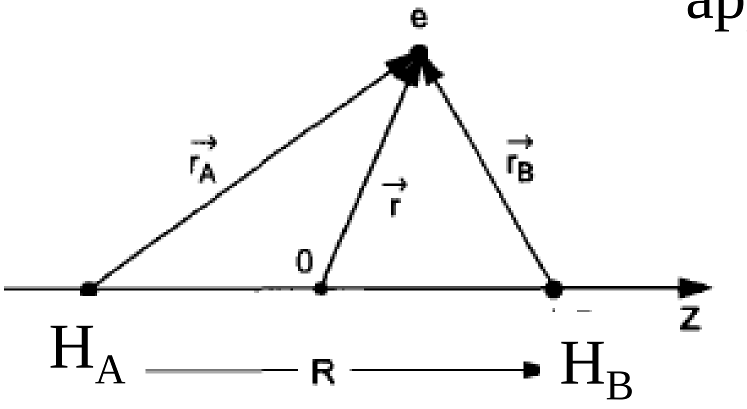
H_2^+ Most Simple Diatom

First find ways to solve the electronic wave function when given distance between to hydrogen nuclei

$$\left[-\frac{1}{2}\nabla^2+\left[\frac{1}{|\mathbf{R}|}-\frac{1}{|\mathbf{r}_A|}-\frac{1}{|\mathbf{r}_B|}\right]\right]\Psi_n^{el}(\mathbf{r};\mathbf{R})=E_n(\mathbf{R})\Psi_n^{el}(\mathbf{r};\mathbf{R})$$

Solve this problem:

1. Use exact solution
2. Use linear combination of atomic orbital approximation



Atomic Orbital Review

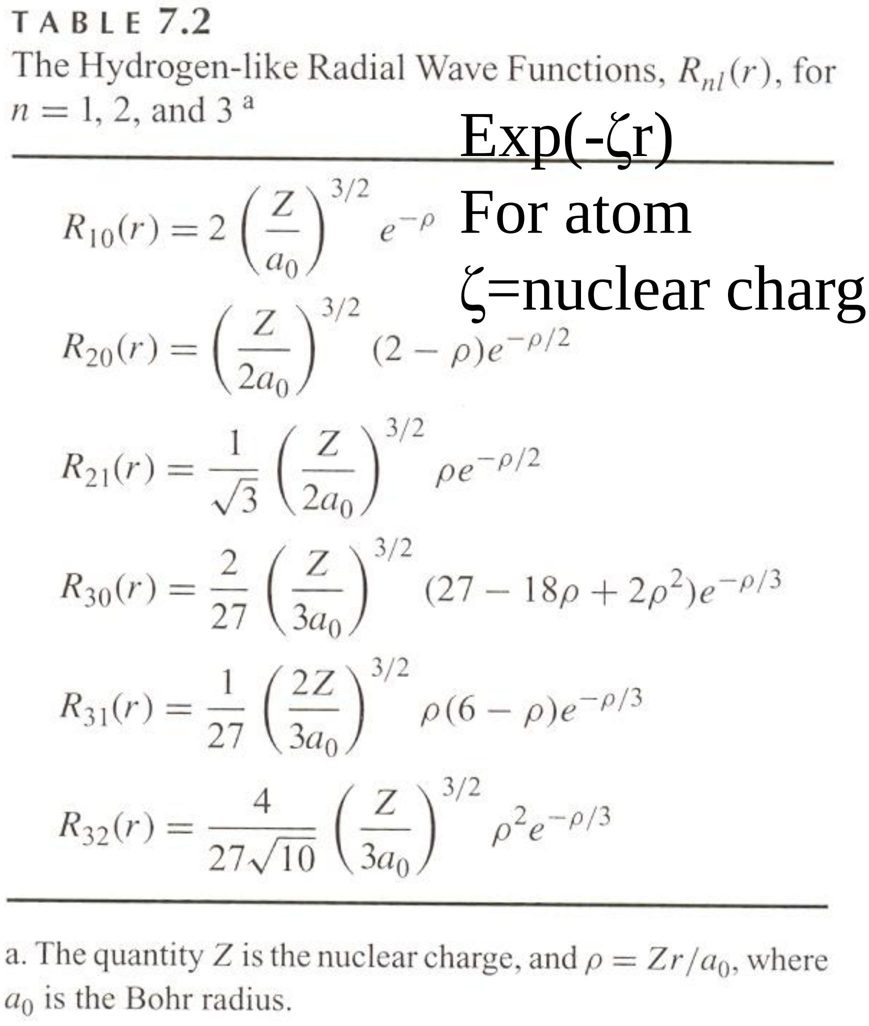


TABLE 7.2

The Hydrogen-like Radial Wave Functions, $R_{nl}(r)$, for $n = 1, 2$, and 3 [a]

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} (2-\rho)e^{-\rho/2}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \rho e^{-\rho/2}$$

$$R_{30}(r) = \frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3}$$

$$R_{31}(r) = \frac{1}{27}\left(\frac{2Z}{3a_0}\right)^{3/2} \rho(6-\rho)e^{-\rho/3}$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2} \rho^2 e^{-\rho/3}$$

---

a. The quantity Z is the nuclear charge, and $\rho = Zr/a_0$, where a_0 is the Bohr radius.

Exp(-ζr)

For atom

ζ=nuclear charge

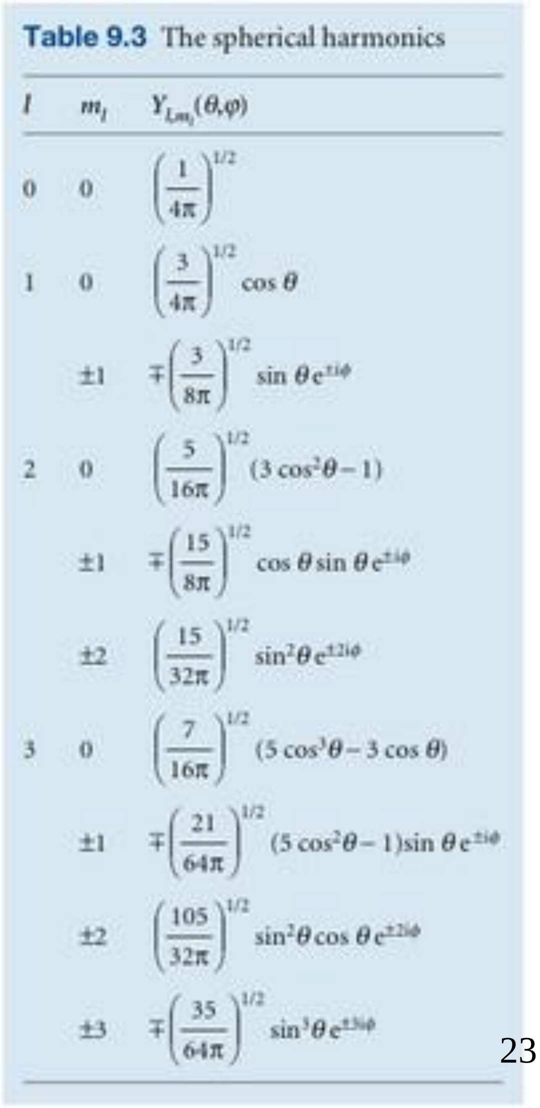
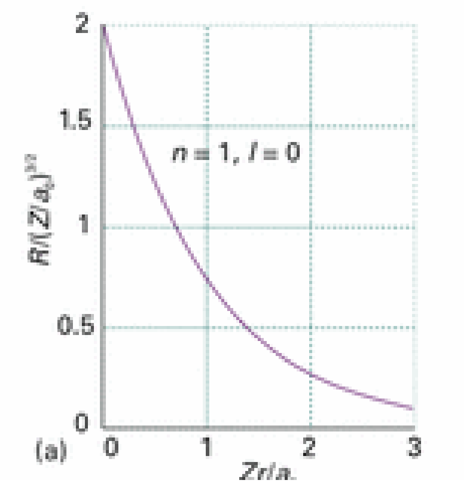
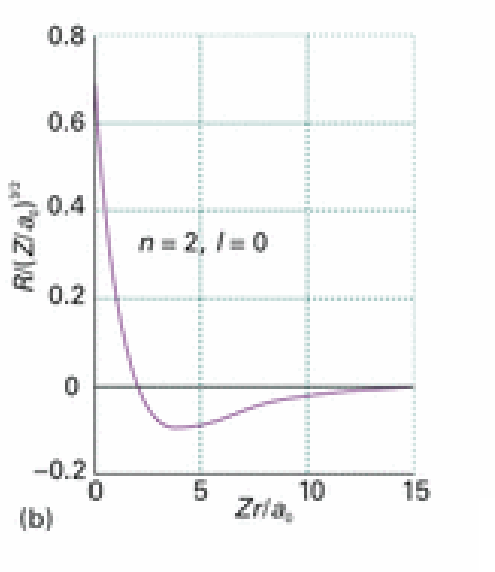


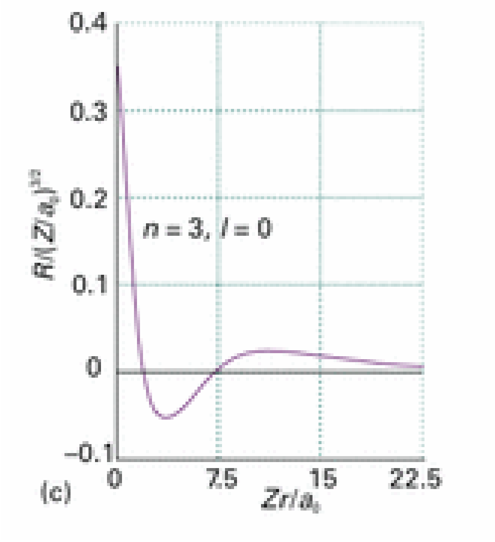
Table 9.3 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

s Wavefunction







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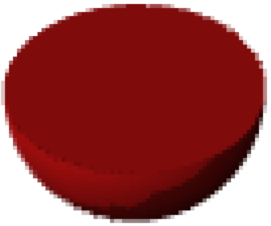
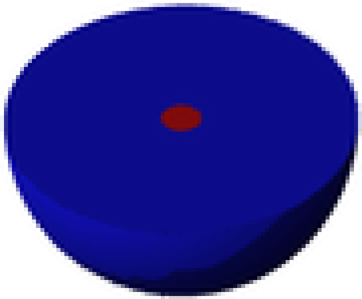
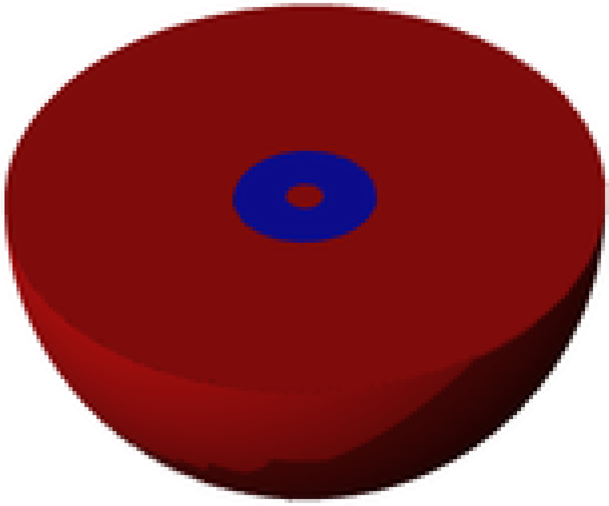
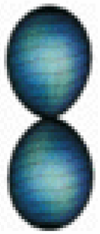


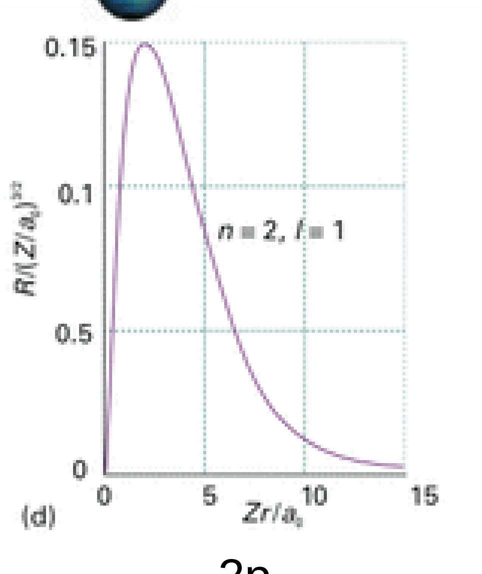
2s

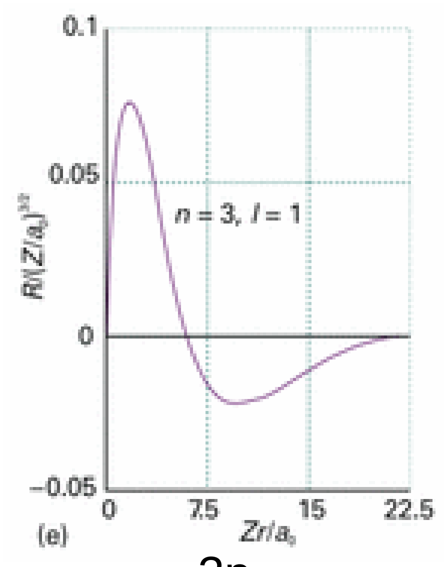






p Wavefunction





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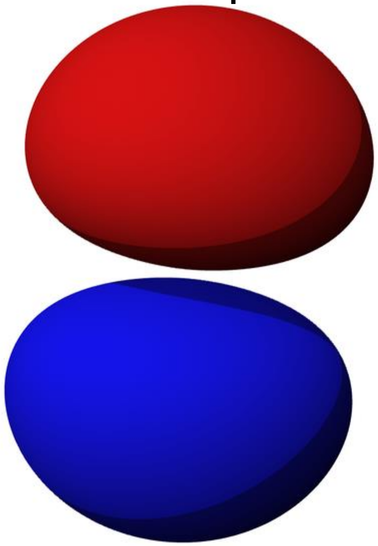

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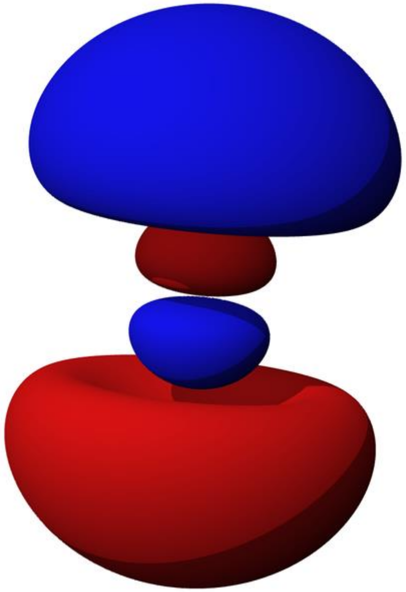

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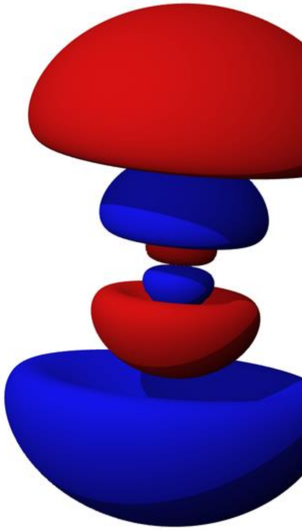
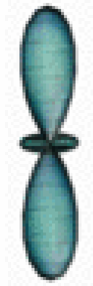
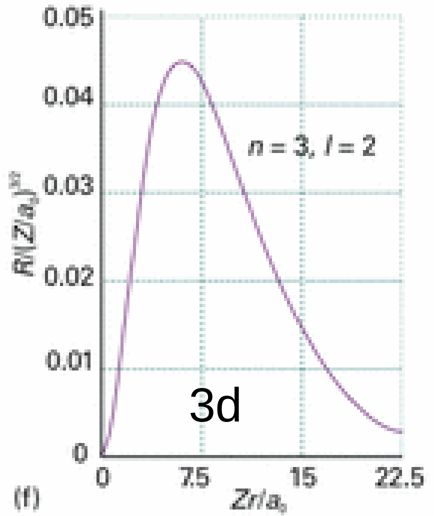
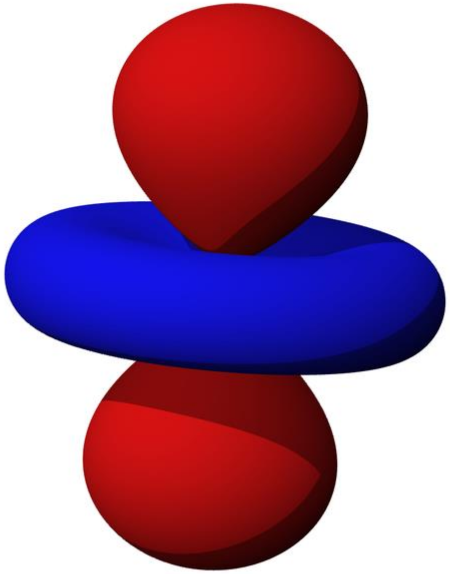




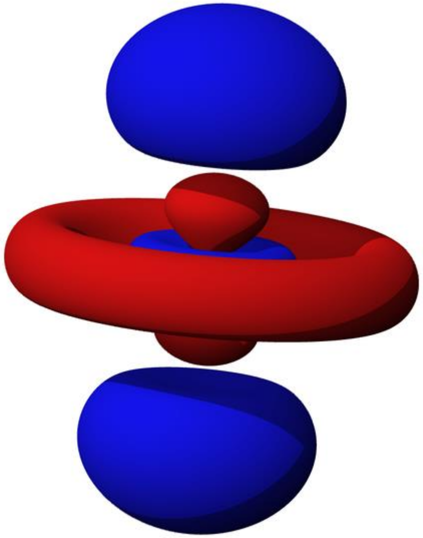
d Wavefunction



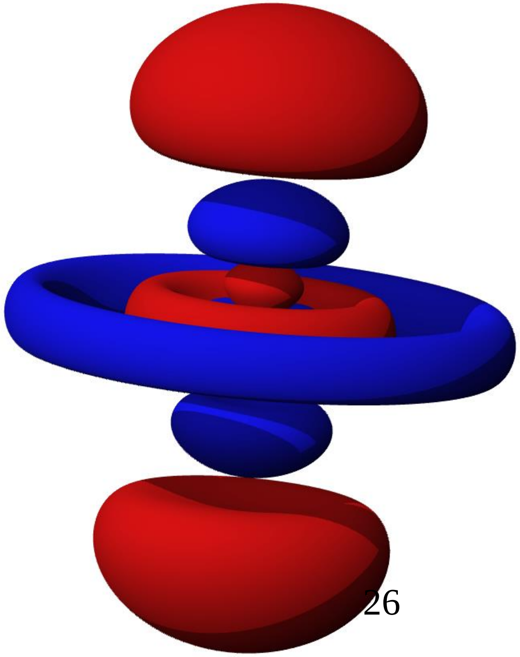
3d



4d



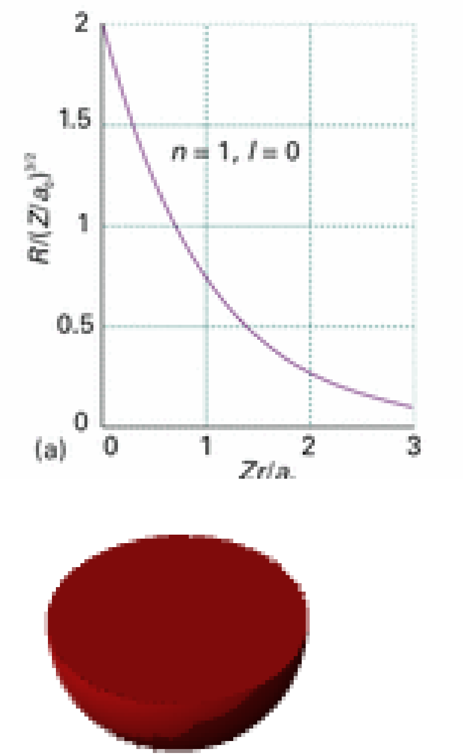
5d

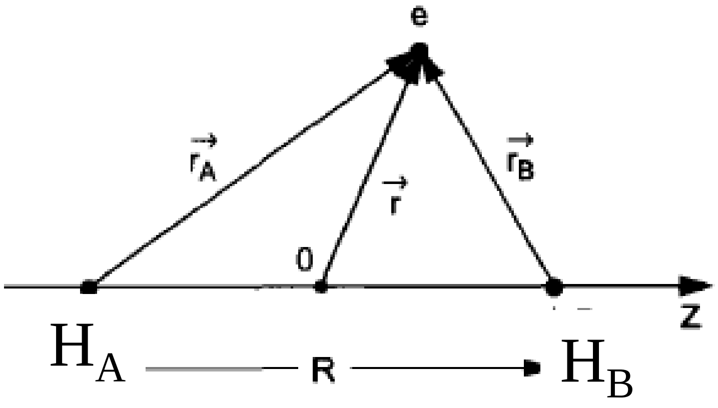


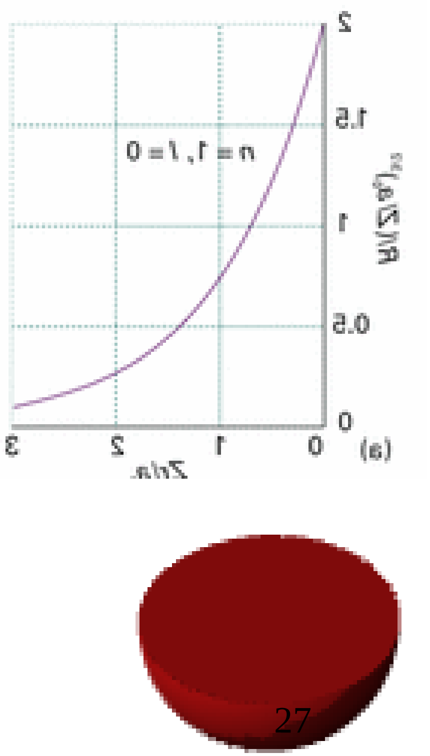
LCAO

To make the molecular orbital (the electronic wavefunction for the molecule) let just add up each atomic orbital (electronic wave function for the atoms making the molecule)

$$\Psi_n^{el}(\mathbf{r}) = C_A\psi_{1S,A}(\mathbf{r}) + C_B\psi_{1S,B}(\mathbf{r})$$







Variational Theory 1

$$E_{exact} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} < E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle}$$

$$\psi_{trial} = \sum_{i=1}^{n} c_i \phi_i \qquad E_{trial} = \frac{\int \sum_{i=1}^{n} c_i{}^* \phi_i{}^* \hat{H} \sum_{j=1}^{n} c_j \phi_j \, d\tau}{\int \sum_{i=1}^{n} c_i{}^* \phi_i{}^* \sum_{j=1}^{n} c_j \phi_j \, d\tau} = \frac{\sum_i \sum_j c_i{}^* H_{ij} c_j}{\sum_i \sum_j c_i{}^* S_{ij} c_j}$$

$$H_{ij} = \int \phi_i{}^* \hat{H} \phi_j \, d\tau$$

$$S_{ij} = \int \phi_i{}^* \phi_j \, d\tau$$

$$\sum_i \sum_j c_i{}^* c_j \left(H_{ij} - E_{trial} S_{ij} \right) = 0$$

Here E_{trial} depends on the value of $c_i{}^*$ or c_j

But H_{ij} and S_{ij} only depend on the basis set ϕ_i

Variational Theory 2

$$\sum_i \sum_j c_i^* c_j \left(H_{ij} - E_{trial} S_{ij}\right) = 0$$

Take derivative with $c_{i'}^*$

$$\sum_j c_j \left(H_{i'j} - E_{trial} S_{i'j}\right) + \sum_i \sum_j c_i^* c_j \left(-\frac{\partial E_{trial}}{\partial c_{i'}^*} S_{ij} \right) = 0$$

Take derivative with $c_{j'}$

$$\sum_i c_i^* \left(H_{ij'} - E_{trial} S_{ij'}\right) + \sum_i \sum_j c_i^* c_j \left(-\frac{\partial E_{trial}}{\partial c_{j'}} S_{ij} \right) = 0$$

Due to stationary condition of the solution

$$\frac{\partial E_{trial}}{\partial c_j} = 0; \qquad \frac{\partial E_{trial}}{\partial c_i^*} = 0$$

Variational Theory

$$\sum_j c_j \left(H_{i'j} - E_{trial} S_{i'j}\right) = 0 \qquad \text{for any } i'$$

$$\sum_i c_i^* \left(H_{ij'} - E_{trial} S_{ij'}\right) = 0 \qquad \text{for any } j'$$

This means that if $c_i \neq 0$ the following secular determinant is zero

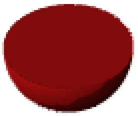
$$\begin{vmatrix} H_{11} - E_{trial} S_{11} & H_{12} - E_{trial} S_{12} & \dots\dots\dots\dots & H_{1n} - E_{trial} S_{1n} \\ H_{21} - E_{trial} S_{21} & H_{22} - E_{trial} S_{22} & \dots\dots\dots\dots & H_{2n} - E_{trial} S_{2n} \\ \dots\dots\dots\dots & \dots\dots\dots\dots & \dots\dots\dots\dots & \dots\dots\dots\dots \\ H_{n1} - E_{trial} S_{n1} & H_{n2} - E_{trial} S_{n2} & \dots\dots\dots\dots & H_{nn} - E_{trial} S_{nn} \end{vmatrix} = 0$$

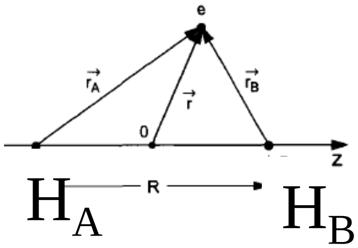
Solving the above equation will give you n values of E_{trial}

Using each value of E_{trial} we obtain c_i $i=1 \rightarrow n$

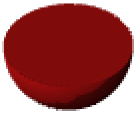
H_2^+

$A\rangle$





$B\rangle$



$$\hat{H}\Psi_n^{el}(\mathbf{r};\mathbf{R}) = \left[-\frac{1}{2}\nabla^2 + \left[\frac{1}{|\mathbf{R}|}-\frac{1}{|\mathbf{r}_A|}-\frac{1}{|\mathbf{r}_B|}\right]\right]\Psi_n^{el}(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\Psi_n^{el}(\mathbf{r};\mathbf{R})$$

$$\Psi_n^{el}(\mathbf{r};R) = C_A\psi_{1S,A}(\mathbf{r};R) + C_B\psi_{1S,B}(\mathbf{r};R) = C_A|A\rangle + C_B|B\rangle$$

$$\begin{vmatrix} H(R)_{AA} - E(R) & H(R)_{AB} - E(R)S(R) \\ H(R)_{BA} - E(R)S(R) & H(R)_{BB} - E(R) \end{vmatrix} = 0$$

$$H(R)_{AA} = \langle A|\hat{H}|A\rangle = \langle B|\hat{H}|B\rangle = H(R)_{BB}$$

$$H(R)_{AB} = \langle A|\hat{H}|B\rangle = \langle B|\hat{H}|A\rangle = H(R)_{BA}$$

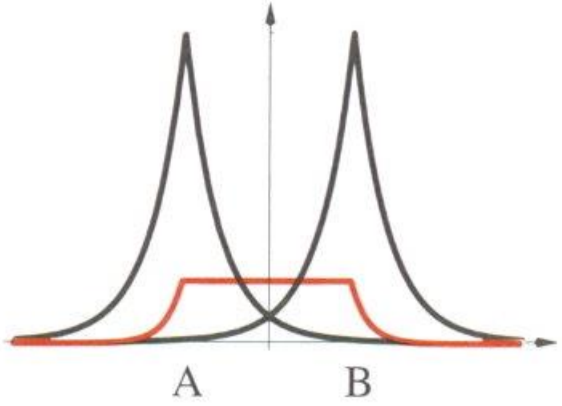
$$S = \langle A|B\rangle = \langle B|A\rangle$$

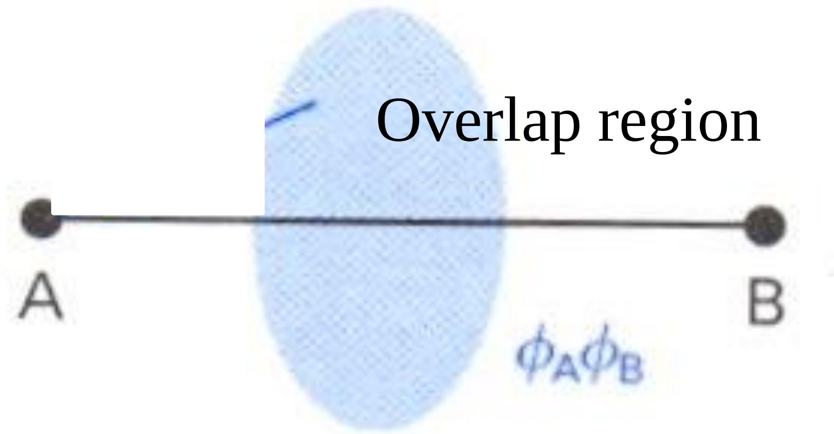
$$\langle A|A\rangle = \langle B|B\rangle = 1$$

Overlap Integral

$$S(R) = \langle A|B\rangle = \langle B|A\rangle$$ Overlap Integral (R dependent)

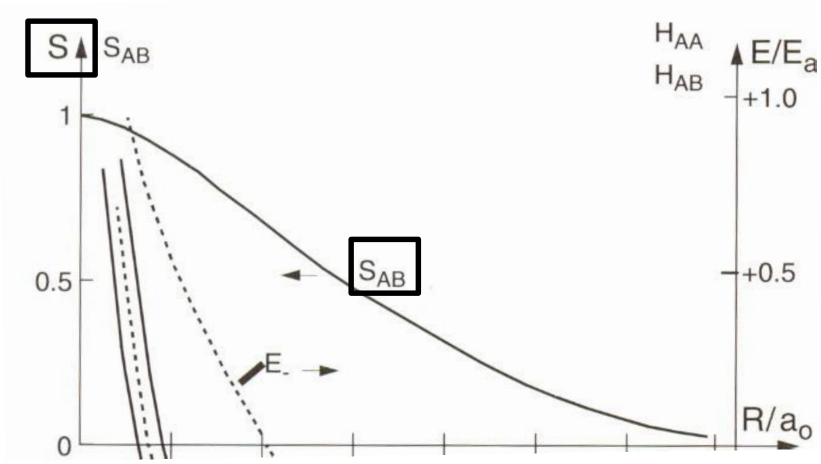
$$S(R) = \int \psi_{1sA}(r;R)\psi_{1sB}(r;R)dr$$





Overlap region

FIGURE 10.9
The overlap of the 1*s* orbitals centered on hydrogen nuclei located at A and B, a distance *R* apart. The orange curve is the product of the two orbitals.



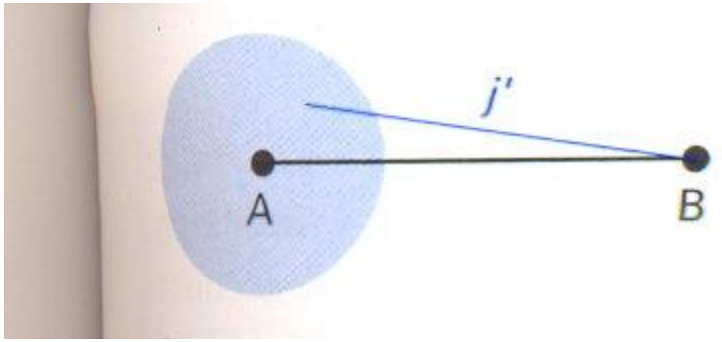
$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

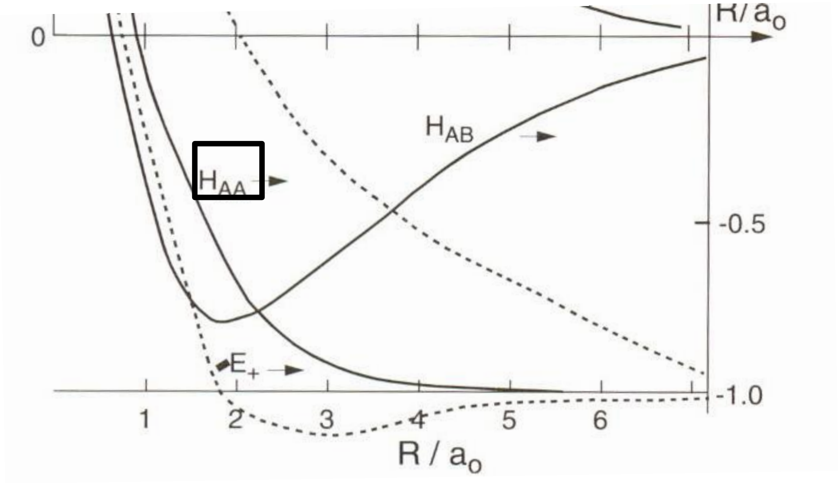
Atomic Integral

$$H(R)_{AA} = \langle A|\hat{H}|A\rangle = \left\langle A \left\| \left[-\frac{1}{2}\nabla^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_A|} - \frac{1}{|\mathbf{r}_B|} \right] \right] \right\| A \right\rangle$$

$$= E_{1S} + \left\langle A \left| -\frac{1}{|\mathbf{r}_B|} \right| A \right\rangle + \frac{1}{|\mathbf{R}|}\langle A | A \rangle = E_{1S} + \left\langle A \left| -\frac{1}{|\mathbf{r}_B|} \right| A \right\rangle + \frac{1}{|\mathbf{R}|}$$

Electron is assigned one of the hydrogen orbitals: Coulomb Integral (Atomic Integral)





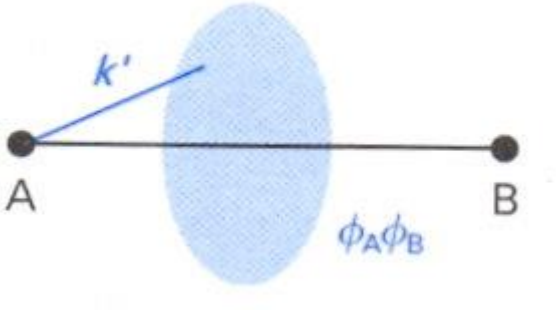
H_{AA} is negative for most regions of R

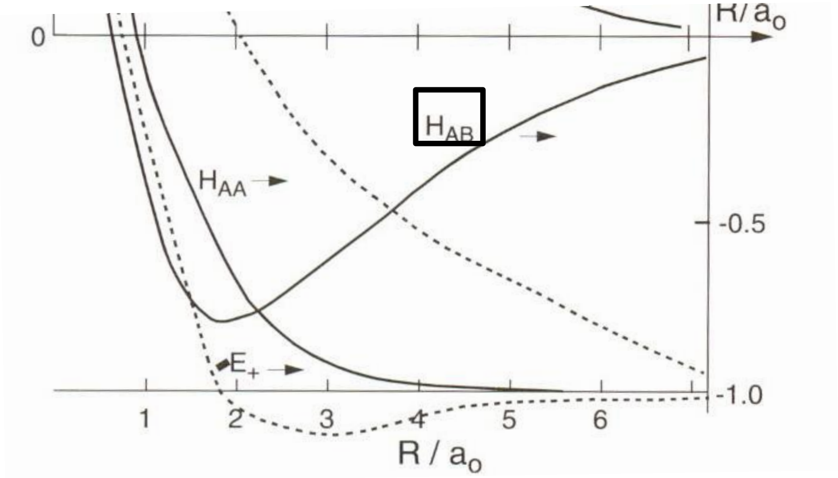
Overlap Charge Integral

$$H(R)_{AB} = \langle A|\hat{H}|B\rangle = \left\langle A\left|\left[-\frac{1}{2}\nabla^2 + \left[\frac{1}{|\mathbf{R}|} - \frac{1}{|\mathbf{r}_A|} - \frac{1}{|\mathbf{r}_B|}\right]\right]\right|B\right\rangle$$

$$= \left\langle A\left|-\frac{1}{2}\nabla^2\right|B\right\rangle + \left\langle A\left|-\frac{1}{|\mathbf{r}_A|}\right|B\right\rangle + \left\langle A\left|-\frac{1}{|\mathbf{r}_B|}\right|B\right\rangle + \frac{1}{|\mathbf{R}|}\langle A|B\rangle$$

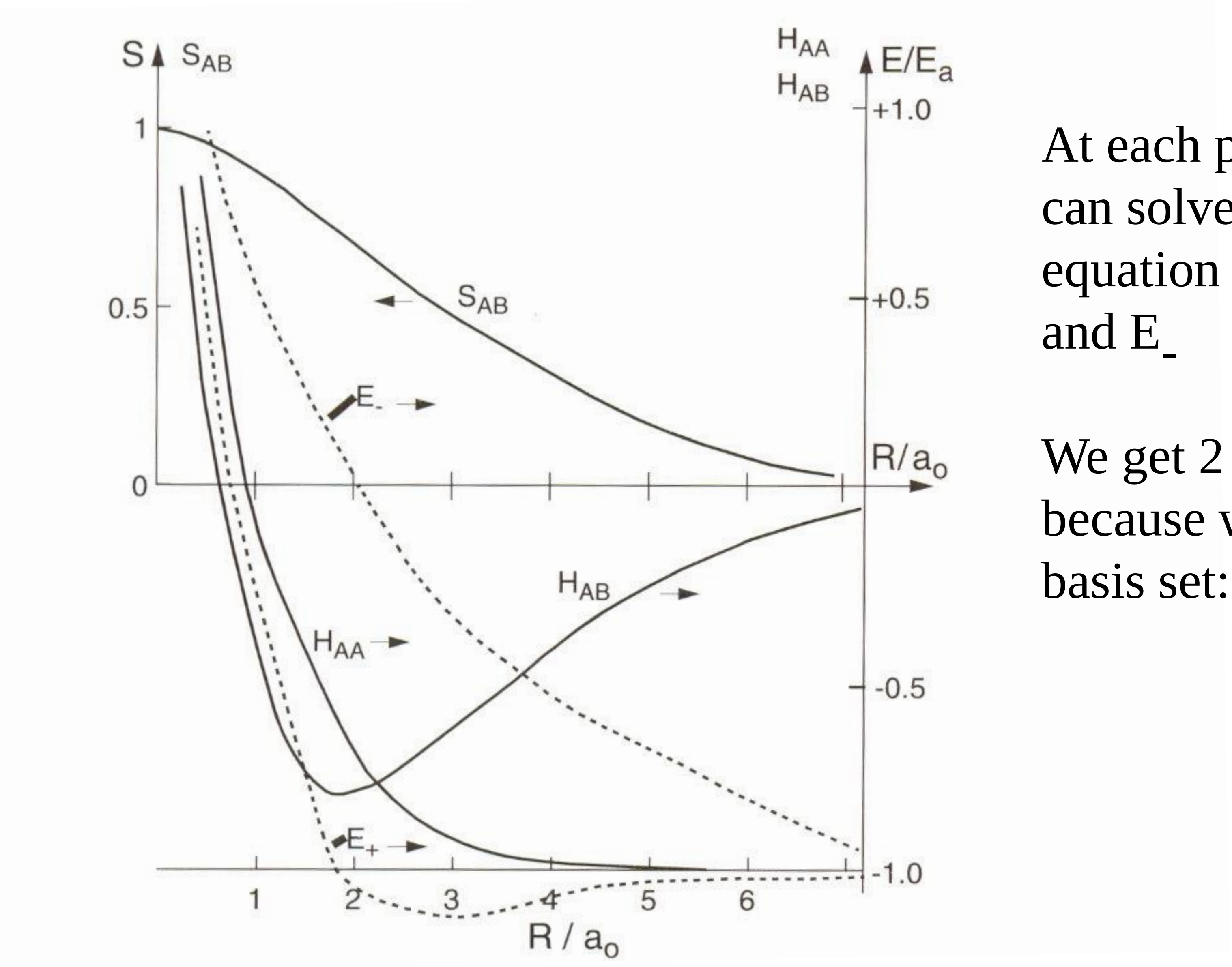
Electron is assigned to both nuclei and we care how much it is overlapped: overlap charge integral





H_{AB} is negative for most regions of R

R Dependence of Matrix Elements



At each point of R we can solve the secular equation and get E_+ and E_-

We get 2 answers because we have 2 basis set: 1sA and 1sB

Dotted lines are the potential energy curve

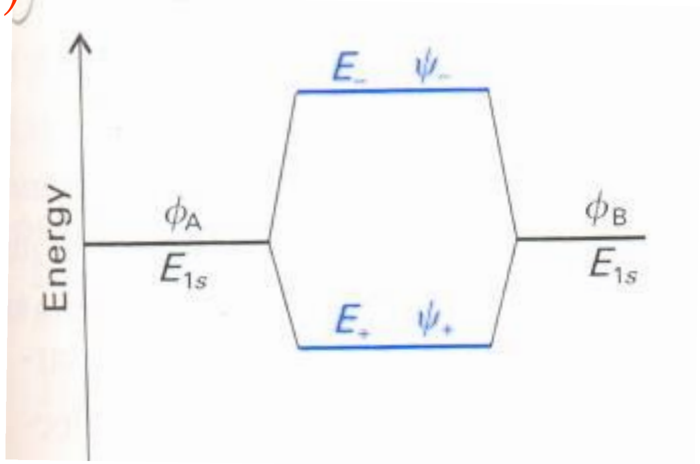
Solve Secular Equation

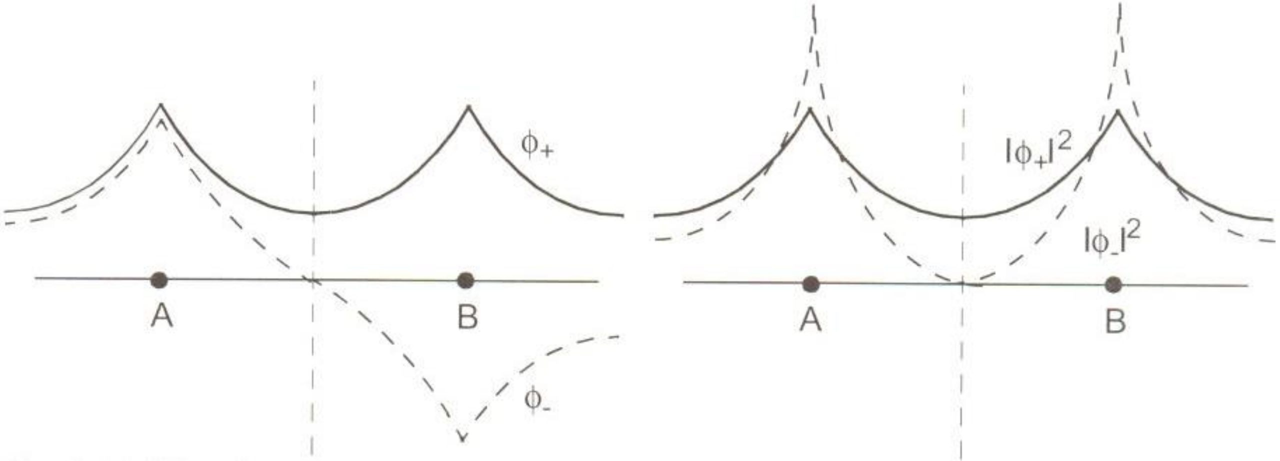
$$\begin{vmatrix} H(R)_{AA}-E(R) & H(R)_{AB}-E(R)S \\ H(R)_{BA}-E(R)S & H(R)_{BB}-E(R) \end{vmatrix}=0$$

$$\left(H(R)_{AA}-E(R)\right)^2-\left(H(R)_{BA}-E(R)S(R)\right)^2=0$$

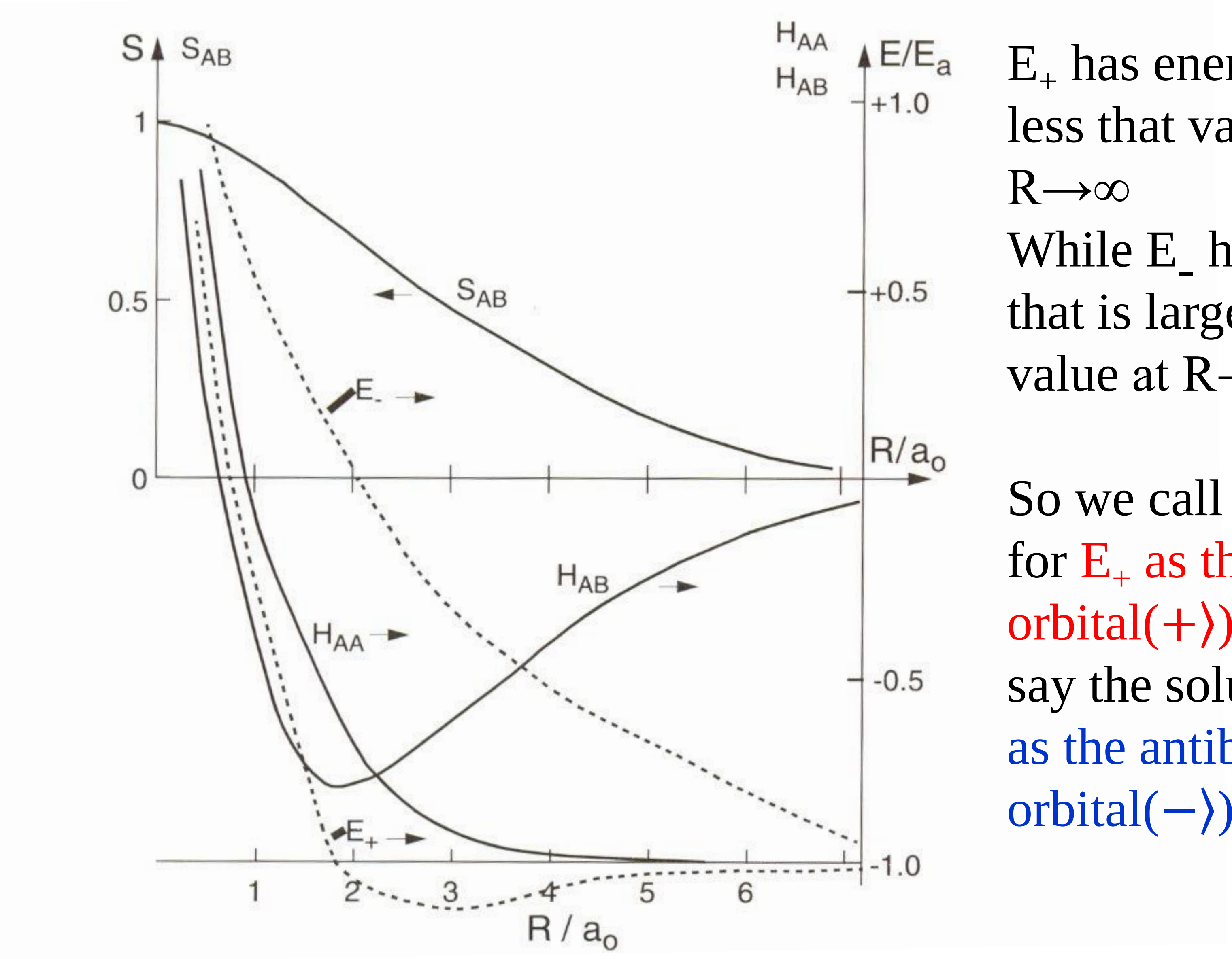
$$E_\pm(R)=\frac{H(R)_{AA}\pm H(R)_{AB}}{1\pm S(R)}$$

$$\Psi_\pm=|\pm\rangle=\frac{|A\rangle\pm|B\rangle}{\sqrt{2\pm2S}}$$





R Dependence of Matrix Elements

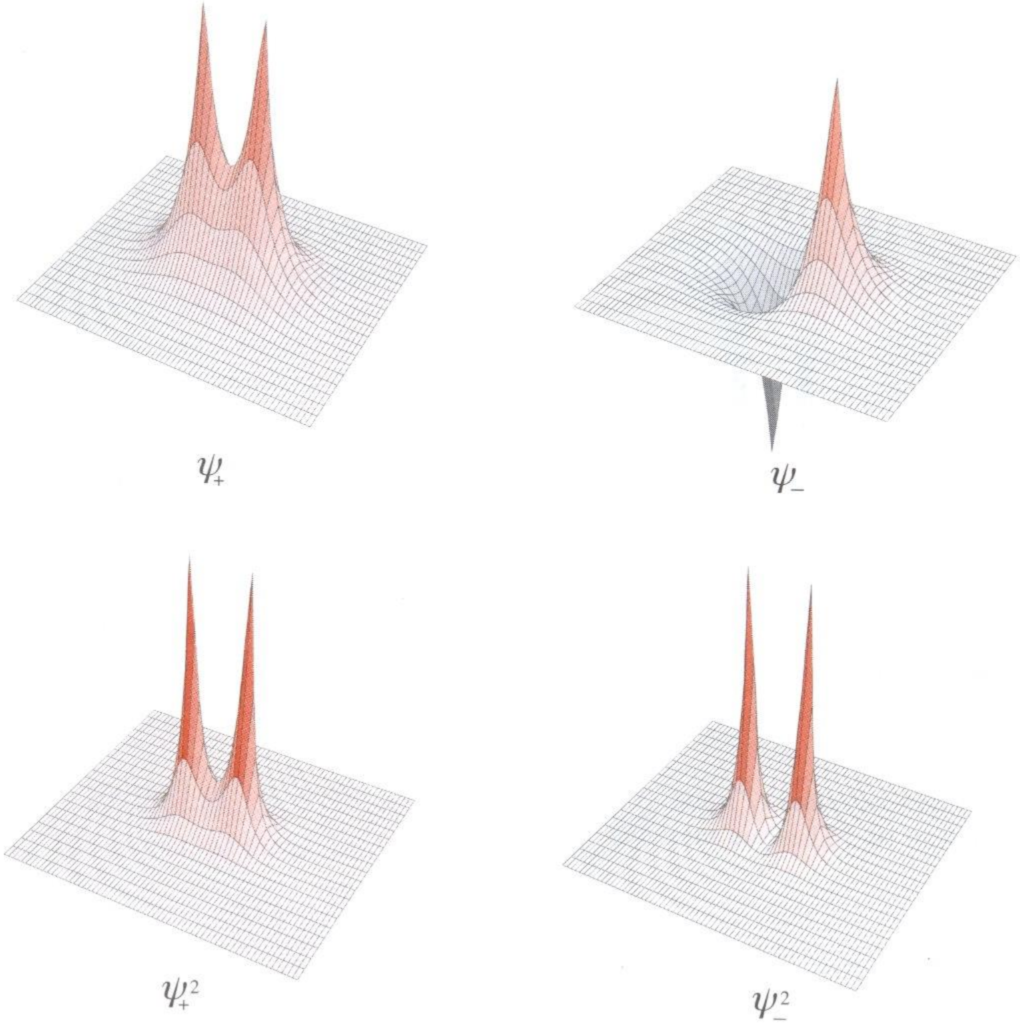


E_+ has energies that is less that value at $R \rightarrow \infty$
While E_- has energies that is larger than value at $R \rightarrow \infty$

So we call the solution for E_+ as the bonding orbital($+\rangle$) while we say the solution for E_- as the antibonding orbital($-\rangle$)

Dotted lines are the potential energy curve

Bonding and Antibonding Orbital



ψ_+ ψ_-

ψ_+^2 ψ_-^2

FIGURE 10.14
Surface plots of the molecular orbitals ψ_+ (a bonding orbital) and ψ_- (an antibonding orbital) and their squares.

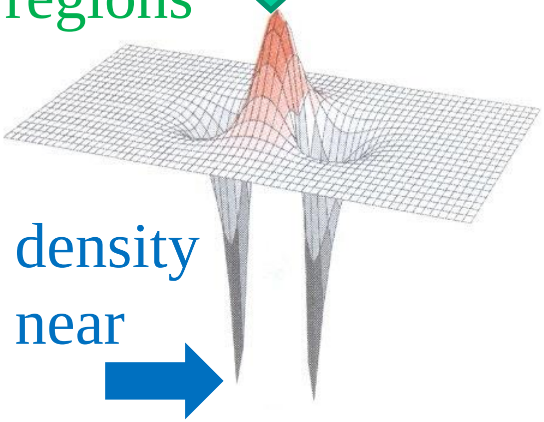
Electron Density Difference

$$\Psi_\pm = \frac{|A\rangle \pm |B\rangle}{\sqrt{2 \pm 2S}} \qquad \text{so} \qquad |\Psi_\pm|^2 = \frac{|A\rangle^2 + |B\rangle^2 \pm 2|A\rangle|B\rangle}{2 \pm 2S}$$

$$|\Psi_{\text{No Bond}}|^2 = \frac{|A\rangle^2 + |B\rangle^2}{2}$$

Subtracting no interaction portion from the bonding and anti bonding orbitals

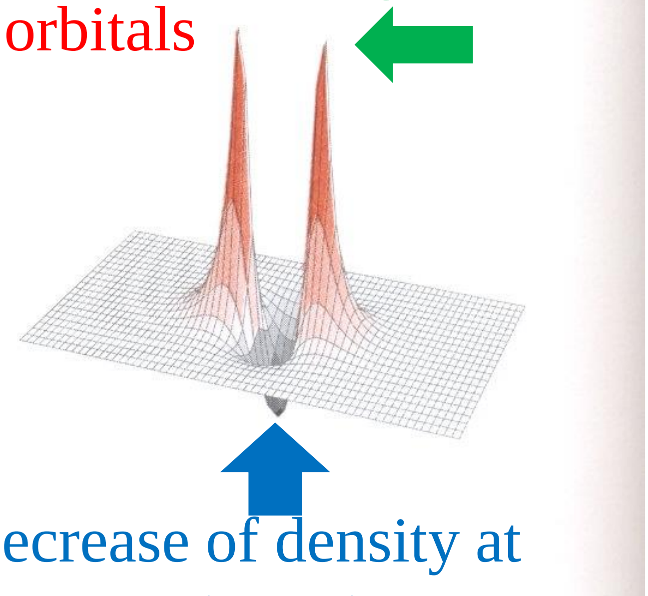
Growth of density at interatomic regions



Decrease of density from region near nucleus

Bonding Orbital

Growth of density at region near nucleus

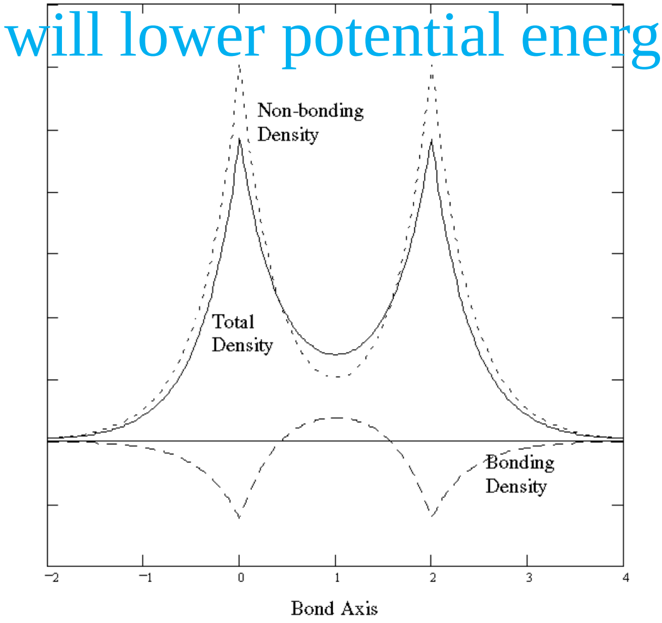


Decrease of density at interatomic region

Antibonding Orbital

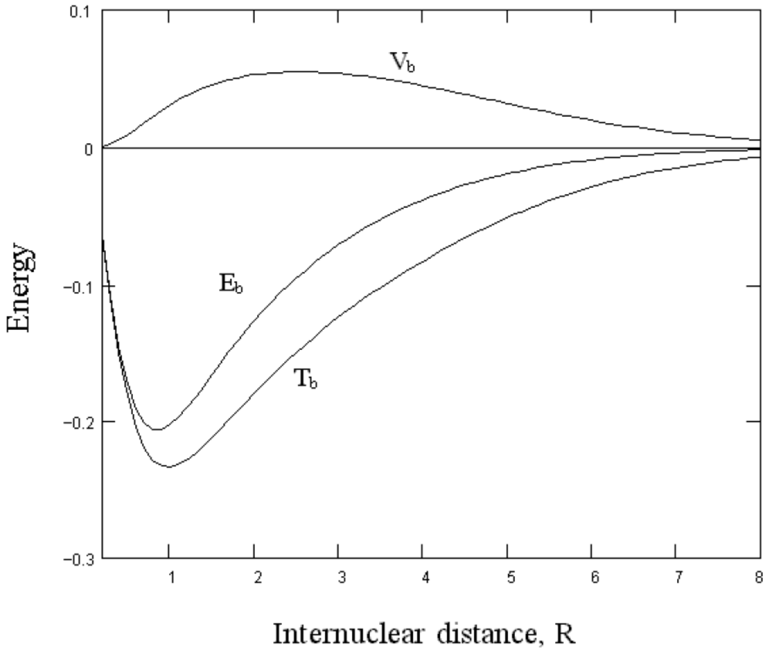
What is the origin for binding?

Charge build up in the region between two nuclei so attracts both positive charge nuclei, seems like it will lower potential energy



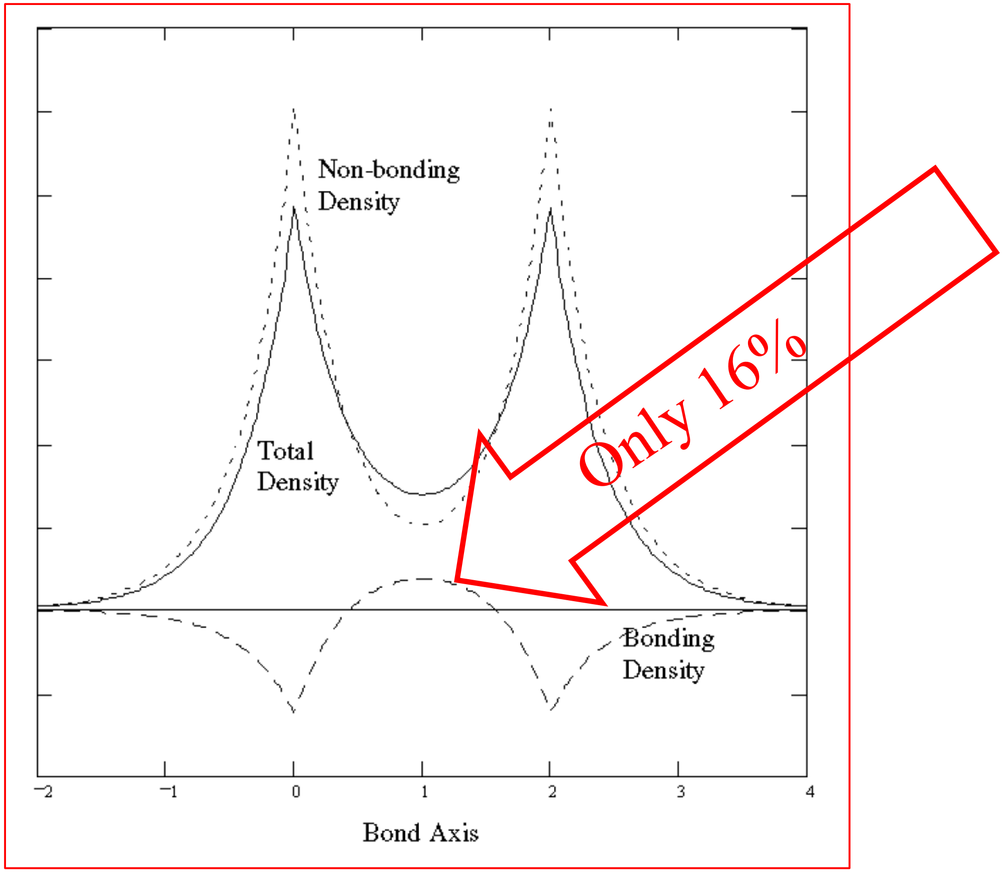
However losing electron density in region near the nuclei center, potential energy increases

Bonding contribution potential versus kinetic energy



Main contribution for stabilization is from kinetic energy! Delocalization causes kinetic energy to decrease greatly

How much electron is transferred?



Only 16%