PHY 742 Quantum Mechanics II
1-1:50 AM MWF Olin 103

Plan for Lecture 9

Single particle states of molecules and solids

1. **Part of this material is mentioned in Chapters 2 and 6 of Professor Carlson's textbook**
   a. **Comparison of the eigenstate analysis of a H atom and an H_2^+ molecular ion**
   b. **Born-Oppenheimer approximation**

Additional references: Ref: Linus Pauling and E. Bright Wilson, "Introduction to Quantum Mechanics", McGraw Hill, 1935, Max Born and Kun Huang, "Dynamical Theory of Crystal Lattices", Oxford, 1954

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Topics for Quantum Mechanics II

Single particle analysis
- **Single particle interacting with electromagnetic fields – EC Chap. 9**
- **Scattering of a particle from a spherical potential – EC Chap. 14**
- **More time independent perturbation methods – EC Chap. 12, 13**
- **Single electron states of a multi-well potential ➔ molecules and solids – EC Chap. 2,6**
- **Time dependent perturbation methods – EC Chap. 15**
- **Path integral formalism (Feynman) – EC Chap. 11.C**
- **Relativistic effects and the Dirac Equation – EC Chap. 16**

Multiple particle analysis
- **Quantization of the electromagnetic fields – EC Chap. 17**
- **Photons and atoms – EC Chap. 18**
- **Multi particle systems; Bose and Fermi particles – EC Chap. 10**
- **Multi electron atoms and materials**
  - **Hartree-Fock approximation**
  - **Density functional approximation**

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Course schedule for Spring 2020

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	Reading	Topic	HW	Due date
1	Mon: 01/13/2020	Chap. 9	Quantum mechanics of electromagnetic forces	#1	01/22/2020
2	Wed: 01/15/2020	Chap. 9	Quantum mechanics of particle in electrostatic field	#2	01/24/2020
3	Fri: 01/17/2020	Chap. 9	Quantum mechanics of particle in magnetostatic field	#3	01/27/2020
	Mon: 01/20/2020	No class	Martin Luther King Holiday		
4	Wed: 01/22/2020	Chap. 14	Scattering theory	#4	01/29/2020
5	Fri: 01/24/2020	Chap. 14	Scattering theory	#5	01/31/2020
6	Mon: 01/27/2020	Chap. 14	Scattering theory	#6	02/03/2020
7	Wed: 01/29/2020	Chap. 12	Variational methods	#7	02/05/2020
8	Fri: 01/31/2020	Chap. 12	Variational and other approximation methods	#8	02/07/2020
9	Mon: 02/03/2020	Chap. 2,6	Single particle states of molecules and solids	#9	02/10/2020
10	Wed: 02/05/2020	Chap. 2,6	H_2^+ molecular ion; Born Oppenheimer approximation	#10	02/12/2020
11	Fri: 02/07/2020				
12	Mon: 02/10/2020				
13	Wed: 02/12/2020				
14	Fri: 02/14/2020				
15	Mon: 02/17/2020				

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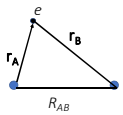
Quantum states of H_2^+



$$r_A \equiv r$$
$$r_B \equiv |\mathbf{r} - \mathbf{R}|$$
$$\mathbf{R}_{AB} \equiv \mathbf{R} = R\hat{\mathbf{z}}$$

Assuming that the nuclear positions are fixed:

Schrödinger equation for electron

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|} + \frac{e^2}{R}$$
$$H\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

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Recall the eigenstates of a H atom --

$$H_{atom} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|} + \frac{e^2}{R}$$

n=5, n=4
n=3
n=2

$$H_{atom}\psi_{atom}(\mathbf{r}) = E_{atom}\psi_{atom}(\mathbf{r})$$
$$\psi_{atom}(\mathbf{r}) \to \psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$$
$$E_{atom} \to E_n = -\frac{e^2}{2a_0 n^2} \qquad n = 1,2,3....$$

n=1

$$\psi_{100}(r) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

Useful basis for representing states of H_2^+ ion

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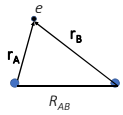

Trial wavefunction:

$$\Psi(\mathbf{r}) = C_A\psi(r_A) + C_B\psi(r_B)$$

where $\psi(r) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$

Note that: $\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right)\psi(r) = \varepsilon_{1s}\psi(r)$

$$\varepsilon_{1s} = -\frac{e^2}{2a_0}$$

Variational estimate of coefficients C_A and C_B :

$$U(C_A, C_B) = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

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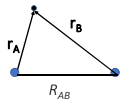

$$\langle\Psi|\Psi\rangle = C_A^2 + C_B^2 + 2C_A C_B \Delta$$

where $\Delta \equiv \int d^3r\ \psi(r_A)\ \psi(r_B) = e^{-D}\left(1 + D + \tfrac{1}{3}D^2\right)$

$$D = R_{AB}/a_0 \equiv R/a_0$$

Some details: Let $s \equiv r/a_0$

$$\int d^3r\ \psi(r_A)\ \psi(r_B) = \frac{2\pi}{\pi}\int_{-1}^{1} dx \int_0^\infty s^2 ds\ e^{-s} e^{-\sqrt{s^2+D^2-2sDx}}$$

$$= 2\int_0^\infty s^2 ds e^{-s} \int_{s+D}^{|s-D|} \frac{udu}{sD} e^{-u} = e^{-D}\left(1 + D + \frac{D^2}{3}\right)$$

$$\langle\Psi|H|\Psi\rangle = C_A^2 H_{AA} + C_B^2 H_{BB} + 2C_A C_B H_{AB}$$

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Optimization wrt coefficients C_A and C_B:

$$U(C_A, C_B) = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

$$\min\left(U(C_A, C_B)\right) \Rightarrow \begin{pmatrix} H_{AA} & H_{AB} \\ H_{AB} & H_{BB} \end{pmatrix}\begin{pmatrix} C_A \\ C_B \end{pmatrix} = U\begin{pmatrix} 1 & \Delta \\ \Delta & 1 \end{pmatrix}\begin{pmatrix} C_A \\ C_B \end{pmatrix}$$

Two solutions:

$$U_+ = \frac{H_{AA} + H_{AB}}{1+\Delta} \qquad \Psi_+(r) = \sqrt{\frac{1}{2(1+\Delta)}}\left(\psi(r_A) + \psi(r_B)\right)$$

$$U_- = \frac{H_{AA} - H_{AB}}{1-\Delta} \qquad \Psi_-(r) = \sqrt{\frac{1}{2(1-\Delta)}}\left(\psi(r_A) - \psi(r_B)\right)$$

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Evaluation of matrix elements:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|} + \frac{e^2}{R}$$

$$H_{AA} = H_{BB} = \langle\psi(r)|H|\psi(r)\rangle$$

$$= \frac{e^2}{2a_0}\left(-1 + \frac{2}{D} - \frac{2}{D} + 2e^{-2D}\left(1 + \frac{1}{D}\right)\right)$$

Note that:

$$\left\langle\psi(r)\left|-\frac{e^2}{|\mathbf{r}-\mathbf{R}|}\right|\psi(r)\right\rangle = -\frac{4e^2}{a_0}\int_0^\infty s^2 ds \frac{1}{s_>} e^{-2s}$$

$$= -\frac{e^2}{a_0 D}\left(1 - e^{-2D}(D+1)\right)$$

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Evaluation of matrix elements – summary --

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|} + \frac{e^2}{R}$$

$$H_{AA} = H_{BB} = \langle \psi(r)|H|\psi(r)\rangle = \frac{e^2}{2a_0}\left(-1 + \frac{2}{D} - \frac{2}{D} + 2e^{-2D}\left(1+\frac{1}{D}\right)\right)$$

$$H_{AB} = H_{BA} = \langle \psi(r)|H|\psi(|\mathbf{r}-\mathbf{R}|)\rangle = \frac{e^2}{2a_0}\left(\left(-1+\frac{2}{D}\right)\Delta - 2e^{-D}(1+D)\right)$$

$$\langle \psi(r)|\psi(|\mathbf{r}-\mathbf{R}|)\rangle \equiv \Delta = e^{-D}\left(1 + D + \frac{D^2}{3}\right)$$

Two solutions:

$$U_+(D) = \frac{H_{AA}+H_{AB}}{1+\Delta} \quad \text{where} \quad \Psi_+(r) = \sqrt{\frac{1}{2(1+\Delta)}}\left(\psi(r_A)+\psi(r_B)\right)$$

$$U_-(D) = \frac{H_{AA}-H_{AB}}{1-\Delta} \quad \text{where} \quad \Psi_-(r) = \sqrt{\frac{1}{2(1-\Delta)}}\left(\psi(r_A)-\psi(r_B)\right)$$

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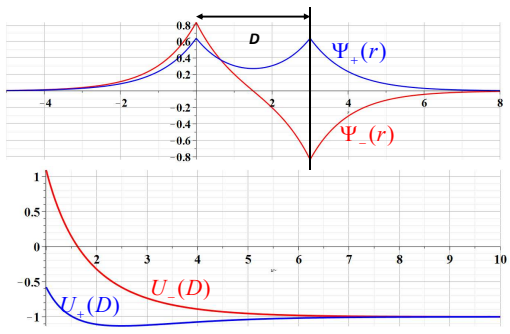

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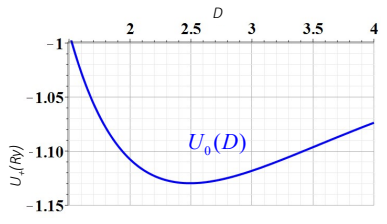

Experimental bond length according to NIST:
~ 2 Bohr

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A more complete treatment, takes into account the effects of nuclear motions --

DYNAMICAL THEORY OF
CRYSTAL LATTICES

BY

MAX BORN

TAIT PROFESSOR OF NATURAL PHILOSOPHY
UNIVERSITY OF EDINBURGH

AND

KUN HUANG

PROFESSOR OF PHYSICS
UNIVERSITY OF PEKING

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Born-Oppenheimer approximation
M. Born and R. Oppenheimer, *Ann. d. Phys.* **84**, 457 (1927)

Total Hamiltonian

$$H = T_E + T_N + U(x, X)$$

Electron kinetic energy; Nuclear kinetic energy; Electron-nuclear coupling

$$H^0 = T_E + U(x, X)$$

Fixed nuclear positions

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Eigenstates of electronic Hamiltonian at fixed *X*:

$$(H^0 - \Phi_n(X))\phi_n(x, X) = 0$$

Full eigenstates:

$$(H - E)\Psi(x, X) = 0;$$

$$\Psi(x, X) = \sum_n \psi_n(X)\phi_n(x, X)$$

Solving for the nuclear functions:

$$(T_N + \Phi_n(X) - E)\psi_n(X) + \sum_{n'} C_{nn'}(X, P)\psi_{n'}(X) = 0,$$

Often neglected

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$$(T_N + \Phi_n(X) - E)\psi_n(X) + \sum_{n'} C_{nn'}(X, P)\psi_{n'}(X) = 0,$$

Nuclear kinetic energy $T_N = \frac{1}{2}\sum_k P_k^2/M_k$

$$C_{nn'} = \sum_k \frac{1}{M_k}\left(A^{(k)}_{nn'} P_k + B^{(k)}_{nn'}\right),$$

$$A^{(k)}_{nn'}(X) = \int \phi_n^*(x, X) P_k \phi_{n'}(x, X)\, dx,$$

$$B^{(k)}_{nn'}(X) = \frac{1}{2}\int \phi_n^*(x, X) P_k^2 \phi_{n'}(x, X)\, dx.$$

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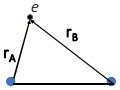
Treatment of nuclear motion



$$\frac{\text{proton mass}}{\text{electron mass}} \approx 2000$$

$$\left(-\frac{\hbar^2}{2M}\nabla_A^2 - \frac{\hbar^2}{2M}\nabla_B^2 + \Phi_n(R_{AB})\right)\psi_{n\kappa}(R_A, R_B) = E\psi_{n\kappa}(R_A, R_B)$$

$$\left(-\frac{\hbar^2}{4M}\nabla_{CM}^2 - \frac{\hbar^2}{M}\nabla_{AB}^2 + \Phi_n(R_{AB})\right)\mathrm{X}(R_{CM})\psi_{n\kappa}(R_{AB})$$

$$= \left(E_{CM} + E_{n\kappa}\right)\mathrm{X}(R_{CM})\psi_{n\kappa}(R_{AB})$$

$$\left(-\frac{\hbar^2}{M}\nabla_{AB}^2 + \Phi_n(R_{AB})\right)\psi_{n\kappa}(R_{AB}) = E_{n\kappa}\psi_{n\kappa}(R_{AB})$$

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$$\left(-\frac{\hbar^2}{M}\nabla_{AB}^2 + \Phi_n(R_{AB})\right)\psi_{n\kappa}(\mathbf{R}_{AB}) = E_{n\kappa}\psi_{n\kappa}(\mathbf{R}_{AB})$$

$$\psi_{n\kappa}(\mathbf{R}_{AB}) = \Upsilon_{n\kappa}(R_{AB})Y_{\kappa\mu}(\hat{\mathbf{R}}_{AB})$$

$$\left(-\frac{\hbar^2}{M}\left(\frac{1}{R_{AB}^2}\frac{d}{dR_{AB}}R_{AB}^2\frac{d}{dR_{AB}} - \frac{\kappa(\kappa+1)}{R_{AB}^2}\right) + \Phi_n(R_{AB})\right)\Upsilon_{n\kappa}(R_{AB})$$

$$= E_{n\kappa}\Upsilon_{n\kappa}(R_{AB})$$

Suppose $\Phi_n(R_{AB}) \approx \Phi_0 + \frac{1}{2}k\left(R_{AB} - R_{AB}^0\right)^2$

Let $R_{AB} = R_{AB}^0 + \rho$

Find $E_{n\kappa\nu} = \frac{\hbar^2}{2MR_{AB}^{0\,2}}\kappa(\kappa+1) + \hbar\sqrt{\frac{k}{M}}\left(\nu + \frac{1}{2}\right) + \ldots$

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NIST data for H_2^+

Diatomic constants for H_2^+

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	ν_{00}
Several other excited states, mostly repulsive. 1												
C $^2\Pi_u$ 2pπ	$(102696._7)$ 2	(266.0_1)	(6.45_4)		(1.899)	(0.075_8)		(0.00039)		(4.19_8)	(C-B)	(8806.3) 2
	↳Bishop, Shih, et al., 1975											
B $^2\Sigma_g^+$ 3dσ	$(93804._5)$ 2	(437.1_5)	(5.24_7)		(1.530)	(0.031_2)		(0.000075)		(4.67_7)	(B-X)	$(92877._4)$
	↳Bishop, Shih, et al., 1975											
A $^2\Sigma_u^+$ 2pσ 3											A ← X	
	↳Richardson, Jefferts, et al., 1968											
State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	ν_{00}
X $^2\Sigma_g^+$ 1sσ	0	$2321._7$ 4	66.2 4	0.6	30.2_1 4 5 6	1.68_5 4	0.6	4		1.052 7 8		
	↳Jefferts, 1969											

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Constants of Diatomic Molecules

Constants of diatomic molecules are provided in tabular form. These data contain a large number of notes and comments. Some comments are embedded directly in the table while others are provided in a list of notes which follows the table. The following quantities are provided:

- State
- Energy, T_e
- ω_e (vibrational constant)
- $\omega_e x_e$ (vibrational constant)
- $\omega_e y_e$ (vibrational constant)
- B_e (rotational constant)
- α_e (rotational constant)
- rotation-vibration interaction constant, γ_e
- D_e (rotational constant)
- β_e
- Internuclear distance in Å, r_e
- Transition
- ν_{00}

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From:

https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=6&ved=0ahUKEwjc7cmpipHXAhVH6SYKHTKqCbkQFghEMAU&url=https%3A%2F%2Fwww.ethz.ch%2Fcontent%2Fdam%2Fethz%2Fspecial-interest%2Fchab%2Fphysical-chemistry%2Fultrafast-spectroscopy-dam%2Fdocuments%2Flectures%2FspectroscopyFS13%2FscriptFS13%2FPCV_Ch3.pdf&usg=AOvVaw3UBFJLJvEzpZNAyr-NHGxl

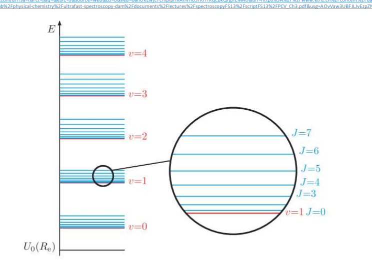

Figure 3.2: Schematic of the rovibronic energy levels of a diatomic molecule.

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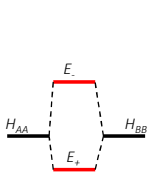
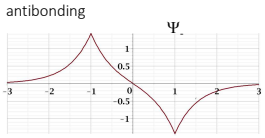
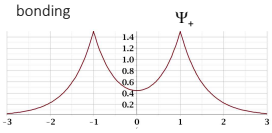
Summary -- Electronic structure of H_2^+ -like molecular ion – continued



antibonding



bonding



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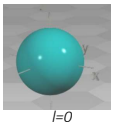
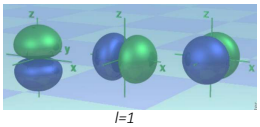
LCAO→Linear Combination of Atomic Orbitals

LCAO methods -- continued – angular varity

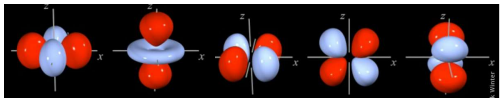
http://winter.group.shef.ac.uk/orbitron/



l=0



l=1



l=2

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LCAO methods -- continued – angular varity

While, for atoms the "z" axis is an arbitrary direction, for diatomic molecules and for describing bonds, it is convenient to take the **"z" axis as the bond direction.**

		Atom *symbol*
l=0	*m=0*	*s*
l=1	*m=0*	*p*
	m= ±1	***p***
l=2	*m=0*	*d*
	m= ± 1	*d*
	m= ± 2	*d*

		Bond *symbol*
l=0	*λ=0*	*σ*
l=1	*λ=0*	*σ*
	λ=1	*π*
l=2	*λ=0*	*σ*
	λ=1	*π*
	λ= 2	*δ*

Here $\lambda \equiv |m|$.

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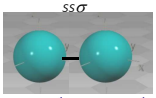
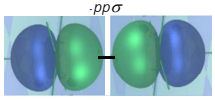
LCAO methods -- continued – bond types

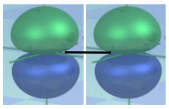
$ss\sigma$



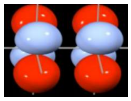
$pp\sigma$



$pp\pi$



$dd\pi$



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