PHY 741 Quantum Mechanics
12-12:50 AM MWF Olin 103

Plan for Lecture 24:

Quantum states of a diatomic molecule

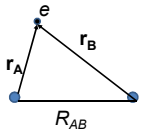
1. H_2^+ with stationary nuclei
2. H_2^+ within Born-Oppenheimer approximation

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

16	Fri, 10/06/2017	Chap. 12-13	Spherically symmetric systems		
17	Mon, 10/09/2017	Chap. 13	Quantum mechanics of a hydrogen atom	#10	10/16/2017
18	Wed, 10/11/2017	Chap. 13	Quantum mechanics of multi-electron atoms		
	Fri, 10/13/2017		*Fall break -- No class*		
19	Mon, 10/16/2017		Discuss exam questions and topics for presentations	Topic	10/18/2017
20	Wed, 10/18/2017	Chap. 14	Intrinsic spin	#11	10/20/2017
21	Fri, 10/20/2017	Chap. 15	Addition of Angular Momentum	#12	10/23/2017
22	Mon, 10/23/2017	Chap. 15	Multi-electron atoms	#13	10/25/2017
23	Wed, 10/25/2017	Chap. 15	Multi-electron atoms	#14	10/30/2017
24	Fri, 10/27/2017		Effects of nuclear motion		
25	Mon, 10/30/2017				
26	Wed, 11/01/2017				
27	Fri, 11/03/2017				
28	Mon, 11/06/2017				
29	Wed, 11/08/2017				
30	Fri, 11/10/2017				
31	Mon, 11/13/2017				
32	Wed, 11/15/2017				
33	Fri, 11/17/2017				

Quantum states of H_2^+



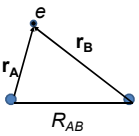
$$r_A \equiv r$$
$$r_B \equiv |\mathbf{r} - \mathbf{R}|$$
$$\mathbf{R}_{AB} \equiv \mathbf{R} = R\hat{\mathbf{z}}$$

Assuming that the nuclear positions are fixed:

Schroedinger equation for electron

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

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r})$$



Trial wavefunction:

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

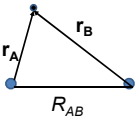
where $\psi(r) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$

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 :

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



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

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

$$D = R / a_0$$

Some details:

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

$$= 2\int_0^\infty r^2 dr e^{-r} \int_{|r-D|}^{r+D} \frac{udu}{rD} e^{-u}$$

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

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:

$$U_0 = \frac{H_{AA} + H_{AB}}{1 + \Delta} \qquad \Psi_0(r) = \sqrt{\frac{1}{2(1+\Delta)}}\left(\psi(r_A) + \psi(r_B)\right)$$

$$U_1 = \frac{H_{AA} - H_{AB}}{1 - \Delta} \qquad \Psi_1(r) = \sqrt{\frac{1}{2(1-\Delta)}}\left(\psi(r_A) - \psi(r_B)\right)$$

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:

$$\langle \psi(r)|-\frac{e^2}{|\mathbf{r}-\mathbf{R}|}|\psi(r)\rangle = -\frac{4e^2}{a_0}\int_0^\infty r^2 dr \frac{1}{r_>}e^{-2r}$$

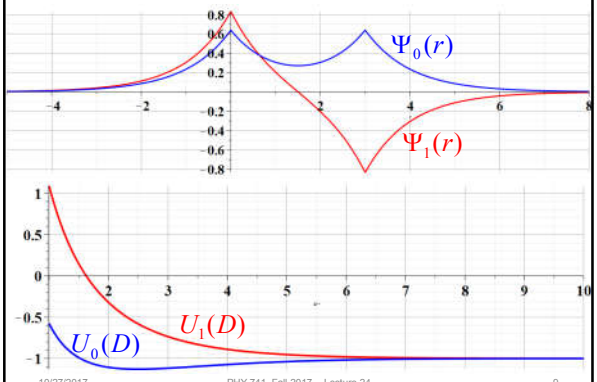
$$= -\frac{e^2}{a_0 D}\left(1 - e^{-2D}(D+1)\right)$$

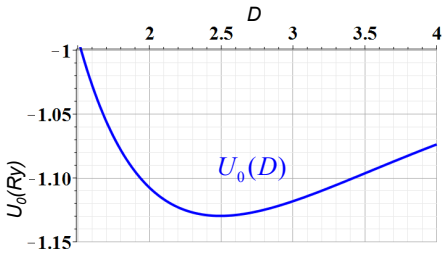
Evaluation of matrix elements -- continued:

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

$$H_{AB} = H_{BA} = \langle \psi(r)|H|\psi(|\mathbf{r}-\mathbf{R}|)\rangle$$

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





Experimental bond length according to NIST:
~ 2 Bohr

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
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PROFESSOR OF PHYSICS
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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 postitions

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

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

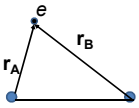
Nuclear kinetic energy $T_N = \frac{1}{2}\sum_k P_k^2/M_k$

$$C_{nn'} = \sum_k \frac{1}{M_k}(A_{nn'}^{(k)} P_k + B_{nn'}^{(k)}),$$

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

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

Treatment of nuclear motion



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

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

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

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

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

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

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

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

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

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

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

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												
$C\,^2\Pi_u\,2p\pi$	$(102696._7)$ 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											
$B\,^2\Sigma_g^+\,3d\sigma$	$(93804._5)$ 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											
$A\,^2\Sigma_u^+\,2p\sigma$ 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}**
$X\,^2\Sigma_g^+\,1s\sigma$	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											

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}

From:

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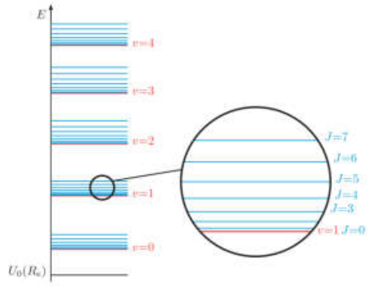

Figure 3.2: Schematic of the rovibronic energy levels of a diatomic molecule.