6.730 Physics for Solid State Applications

Lecture 2: Vibrational and Rotational States in Hydrogen

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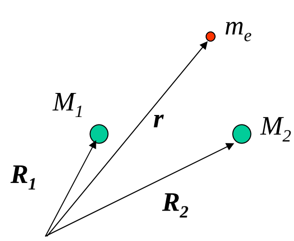
Review Lecture 1: H_2

$\psi(\mathbf{r}, \mathbf{R_1}, \mathbf{R_2})$, the wavefunction for the entire system of nuclei and electrons



$$\hat{\mathcal{H}}\psi(\mathbf{r}, \mathbf{R_1}, \mathbf{R_2}) = \mathbf{E}\psi(\mathbf{r}, \mathbf{R_1}, \mathbf{R_2})$$

$$\hat{\mathcal{H}} = \frac{|\mathbf{P_1}|^2}{2M_1} + \frac{|\mathbf{P_2}|^2}{2M_2} + \frac{|\mathbf{p}|^2}{2m_e} - \frac{e^2}{4\pi\epsilon_o|\mathbf{r}-\mathbf{R_1}|} - \frac{e^2}{4\pi\epsilon_o|\mathbf{r}-\mathbf{R_2}|} + \frac{e^2}{4\pi\epsilon_o|\mathbf{R_1}-\mathbf{R_2}|}\,.$$

Approximate Models: Simplifying H_2

Born-Oppenheimer Approximation

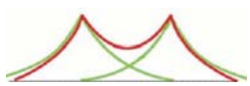
- The electrons are much lighter than the nuclei ($m_e/m_H \cong 1/1836$), their motion is much faster than the vibrational and rotational motions of the nuclei within the molecule.

➔ Works since vibrational and rotational energy of molecule is typically much less than the binding energy

$$\Psi(\mathbf{r},\mathbf{R}_1,\mathbf{R}_2) \approx \Phi(\mathbf{R}_1,\mathbf{R}_2)\psi(\mathbf{r};\mathbf{R}_1,\mathbf{R}_2)\,.$$

Linear Combination of Atomic Orbitals (LCAO)

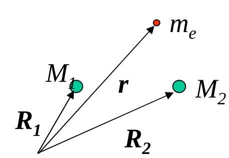
Even the electron part of the problem is too hard to solve exactly



$$\psi(\mathbf{r};\mathbf{R}_1,\mathbf{R}_2) = \mathbf{C}\left[\phi_{1s}(\mathbf{r}-\mathbf{R}_1)+\phi_{1s}(\mathbf{r}-\mathbf{R}_2)\right]$$

Born-Oppenheimer Approximation

$$\Psi(\mathbf{r},\mathbf{R}_1,\mathbf{R}_2) \approx \Phi(\mathbf{R}_1,\mathbf{R}_2)\psi(\mathbf{r};\mathbf{R}_1,\mathbf{R}_2)$$



Electronic Part: $\psi(\mathbf{r};\mathbf{R}_1,\mathbf{R}_2) \longrightarrow \psi(\mathbf{r})$ with $\mathbf{R}_1$ and $\mathbf{R}_2$ fixed

$$E_e(\mathbf{R}_1,\mathbf{R}_2)\psi(\mathbf{r}) = \underbrace{\left[-\frac{\hbar^2\nabla^2}{2m_e} - \frac{e^2}{4\pi\epsilon_o|\mathbf{r}-\mathbf{R}_1|} - \frac{e^2}{4\pi\epsilon_o|\mathbf{r}-\mathbf{R}_2|}\right]}_{\hat{\mathcal{H}}_e}\psi(\mathbf{r})$$

Nuclear Part:

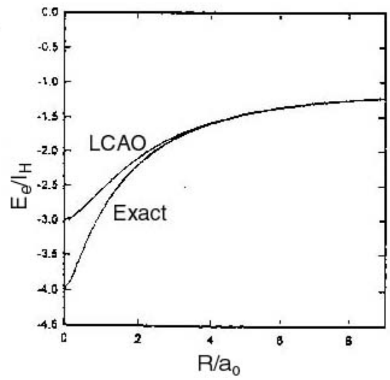
$$E\Phi(\mathbf{R}_1,\mathbf{R}_2) = \left[-\frac{\hbar^2\nabla_1^2}{2\mathrm{M}_1} - \frac{\hbar^2\nabla_2^2}{2\mathrm{M}_2} + \underbrace{E_e(\mathbf{R}_1,\mathbf{R}_2) + \frac{\mathrm{e}^2}{4\pi\epsilon_o|\mathbf{R}_1-\mathbf{R}_2|}}_{\mathrm{V_{eff}}}\right]\Phi(\mathbf{R}_1,\mathbf{R}_2)$$

where *E* is the energy of the <u>entire</u> molecule

Approximate Electronic Energy

$$E_e(R) = \frac{E_s + V_{ss\sigma}}{1 + S(1)} \qquad E_s(R) = E_s^o + \left\langle \phi_1(\mathbf{r}) | \widehat{V}_2 | \phi_1(\mathbf{r}) \right\rangle$$

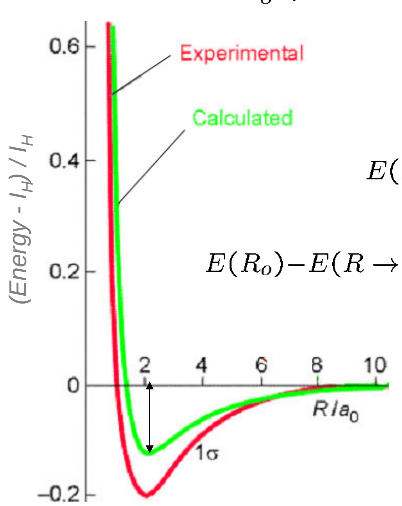
$$E_s^o = -I_H = -m_e e^4 / (32\pi^2 \epsilon_o^2 \hbar^2) = -13.6\,\text{eV}$$



Nuclear and Electronic Energy Together

$$V_{\text{eff}} = E_e(R) + \frac{e^2}{4\pi\epsilon_o R}$$

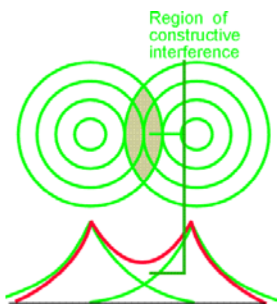
$$E\Phi(\mathrm{R}_1,\mathrm{R}_2) = \left[-\frac{\hbar^2\nabla_1^2}{2\mathrm{M}_1} - \frac{\hbar^2\nabla_2^2}{2\mathrm{M}_2} + \underbrace{E_e(\mathrm{R}_1,\mathrm{R}_2) + \frac{\mathrm{e}^2}{4\pi\epsilon_o|\mathrm{R}_1 - \mathrm{R}_2|}}_{\mathrm{V_{eff}}} \right] \Phi(\mathrm{R}_1,\mathrm{R}_2)$$

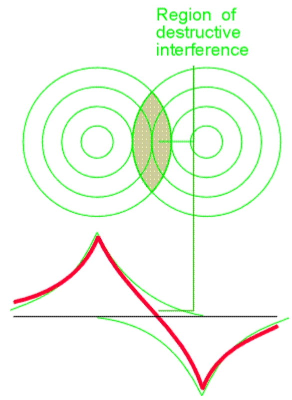


$$E(R_o) = V_{\text{eff}}[LCAO](R_o) = -1.13\, I_H$$

$$E(R_o) - E(R \to \infty) = -0.1\, I_H = -1.4\,\text{eV per bond}$$

First Excited State Energy: Antibonding

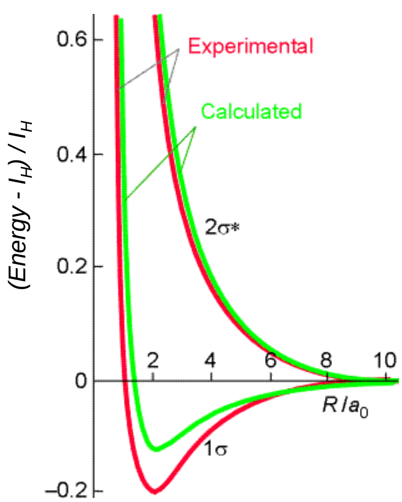


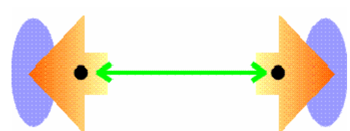


$$\psi_{1\sigma g}(\mathbf{r}) = \mathbf{C}\left[\phi(\mathbf{r}-\mathbf{R}_1) + \phi(\mathbf{r}-\mathbf{R}_2)\right] \qquad \psi_{1\sigma \mathrm{u}}(\mathbf{r}) = \mathbf{C}\left[\phi(\mathbf{r}-\mathbf{R}_1) - \phi(\mathbf{r}-\mathbf{R}_2)\right]$$

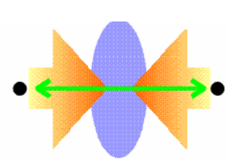
$$E_{e,1\sigma g}(R) = \frac{E_s + V_{ss\sigma}}{1 + S(1)} \qquad E_{e,1\sigma u}(R) = \frac{E_s - V_{ss\sigma}}{1 - S(1)}$$

First Excited State Energy: LCAO





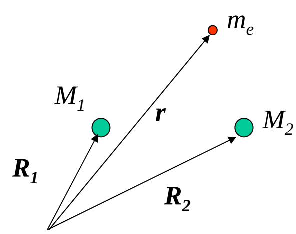
Decrease of electron density



Increase of electron density

A Closer Look at Nuclear Motion

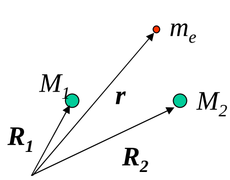
Molecular Vibration and Rotation



$$E\Phi(\mathbf{R_1},\mathbf{R_2}) = \left[\frac{|\mathbf{P}|_1^2}{2\mathbf{M_1}} + \frac{|\mathbf{P}|_2^2}{2\mathbf{M_2}} + \mathbf{V}_{\text{eff}}(|\mathbf{R_1}-\mathbf{R_2}|)\right]\mathbf{\Phi}(\mathbf{R_1},\mathbf{R_2})$$

LCAO for electron in V_{eff}

Divide and Conquer



$$\Psi(\mathbf{r},\mathbf{R_1},\mathbf{R_2})$$

Born-Oppenheimer

$$\Phi(\mathbf{R_1},\mathbf{R_2})\psi(\mathbf{r};\mathbf{R_1},\mathbf{R_2})$$

Center-of-mass and Relative nuclear motion

LCAO for electron in V_{eff}

$$C\,[\phi_1+\phi_2]$$

$$F(\mathbf{R})\phi_{\mathbf{nlm}}(\mathbf{r},\theta,\phi)$$

Vibrational and rotational motion

$$\frac{P_{nl}(r)}{r}Y_{lm}(\theta,\phi)$$

Center-of-Mass and Relative Nuclear Motion

$$E\Phi(\mathbf{R}_1,\mathbf{R}_2) = \left[\frac{|\mathbf{P}|_1^2}{2\mathbf{M}_1} + \frac{|\mathbf{P}|_2^2}{2\mathbf{M}_2} + \mathbf{V}_{\text{eff}}(|\mathbf{R}_1 - \mathbf{R}_2|)\right]\mathbf{\Phi}(\mathbf{R}_1,\mathbf{R}_2)$$

$$E\Phi(\mathbf{r},\mathbf{R}) = \left[\frac{|\mathbf{P}|^2}{2\mathbf{M}} + \frac{|\mathbf{p}|^2}{2\mu} + \mathbf{V}_{\text{eff}}(|\mathbf{r}|)\right]\mathbf{\Phi}(\mathbf{r},\mathbf{R})$$

Center-of-mass

$$M\mathbf{R} = \mathbf{M_1R_1} + \mathbf{M_2R_2}$$

Note that R is the C-of-M coordinate now

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$$

$$M = M_1 + M_2$$

Relative

$$\mathbf{r} = \mathbf{R}_2 - \mathbf{R}_1$$

$$\frac{\mathbf{p}}{\mu} = \frac{\mathbf{P}_2}{M_2} - \frac{\mathbf{P}_1}{M_1}$$

$$\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$$

Center-of-Mass and Relative Nuclear Motion

$$E\Phi(\mathbf{r},\mathbf{R}) = \left[\frac{|\mathbf{P}|^2}{2\mathbf{M}} + \frac{|\mathbf{p}|^2}{2\mu} + \mathbf{V}_{\text{eff}}(|\mathbf{r}|)\right]\mathbf{\Phi}(\mathbf{r},\mathbf{R})$$

$$\mathbf{\Phi}(\mathbf{r},\mathbf{R}) = \mathbf{F}(\mathbf{R})\phi(\mathbf{r})$$

$$E_{\mathbf{R}}F(\mathbf{R}) = \frac{|\mathbf{P}|^2}{2\mathbf{M}}\mathbf{F}(\mathbf{R})$$

$$E_{\mathbf{r}}\phi(\mathbf{r}) = \left[\frac{|\mathbf{p}|^2}{2\mu} + \mathbf{V}_{\text{eff}}(|\mathbf{r}|)\right]\phi(\mathbf{r})$$

Total energy is the sum of CM motion and relative:

$$E = E_{\mathbf{R}} + E_{\mathbf{r}}$$

If this is the total energy, where is the electron energy ?

Center-of-Mass Nuclear Motion

Schrodinger equation for center-of-mass
is same as free particle:

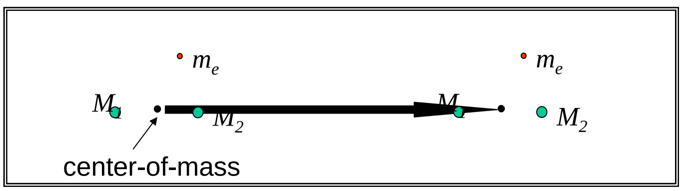
$$E_{\mathrm{R}} F(\mathbf{R}) = \frac{|\mathbf{P}|^2}{2\mathbf{M}} \mathbf{F}(\mathbf{R})$$

Eigenstate:

$$F(\mathbf{R}) = \mathrm{e}^{\mathbf{iK \cdot R}}$$

Eigenenergy:

$$E_{\mathbf{R}} = \frac{\hbar^2 |\mathbf{K}|^2}{2M}$$



Relative Nuclear Motion

Schrodinger equation for relative motion
is a central potential problem just like the hydrogen atom:

$$E_{\mathbf{r}} \phi(\mathbf{r}) = \left[\frac{|\mathbf{p}|^2}{2\mu} + \mathbf{V}_{\text{eff}}(|\mathbf{r}|) \right] \phi(\mathbf{r})$$

$$E_{\mathbf{r}} \phi(r,\theta,\phi) = \left[\frac{p_r^2}{2\mu} + \frac{|\mathbf{L}(\theta,\phi)|^2}{2\mu r^2} + V_{\text{eff}}(r) \right] \phi(r,\theta,\phi)$$

Radial kinetic energy

Angular kinetic energy

$\mathbf{L}(\theta,\phi)$ is the angular momentum operator

Relative Nuclear Motion

Separation of Radial and Angular Components

$$E_{\mathbf{r}}\phi(r,\theta,\phi) = \left[\frac{p_r^2}{2\mu} + \frac{|\mathbf{L}(\theta,\phi)|^2}{2\mu r^2} + V_{\text{eff}}(r)\right]\phi(r,\theta,\phi)$$

$$\phi_{nlm}(r,\theta,\phi) = \frac{P_{nl}(r)}{r}Y_{lm}(\theta,\phi)$$

$Y_{lm}(\theta,\phi)$ is the spherical Bessel function

$$|\mathbf{L}(\theta,\phi)|^2\,\mathbf{Y_{lm}}(\theta,\phi) = \hbar^2 \mathbf{l}(\mathbf{l}+\mathbf{1})\,\mathbf{Y_{lm}}(\theta,\phi)$$

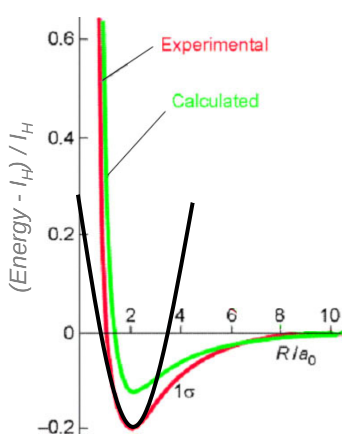
$$E_{\mathbf{r}}P_{nl}(r) = \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V_{\text{eff}}(r)\right]P_{nl}(r)$$

Vibrational Motion of Nuclei

Harmonic Oscillator

For *no* rotation, this simplifies to…

$$E_{\mathbf{r}}^{n0}P_{n0}(r) = \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_{\text{eff}}(r)\right]P_{n0}(r)$$



$$V_{\text{eff}}(r) = V_o + \frac{1}{2}(r-R_o)^2\left(\frac{d^2V}{dr^2}\right)_{R_o}$$

Vibrational Motion of Nuclei

Harmonic Oscillator

$$E_{\mathrm{r}}^{n0} P_{n0}(r) = \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_o + \frac{1}{2}(r-R_o)^2 \left(\frac{d^2V}{dr^2}\right)_{R_o} \right] P_{n0}(r)$$

$$x = r - R_o \qquad \frac{1}{2}(r-R_o)^2 \left(\frac{d^2V}{dr^2}\right)_{R_o} = \frac{1}{2}\mu\omega_o^2 x^2$$

$$\left[E_{\mathrm{r}}^{n0} - V_o\right] P_{n0}(x) = \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}\mu\omega_o^2 x^2 \right] P_{n0}(x)$$

$$\boxed{E_{\mathrm{r}}^{n0} = V_o + \hbar\omega_o(n + \frac{1}{2})}$$

Approximation: Born-Oppenheimer, parabolic effective potential

Vibrational Motion of Nuclei

Rigid Rotor

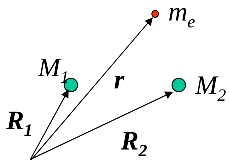
$$E_{\mathrm{r}}^{nl} P_{nl}(r) = \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V_o + \frac{1}{2}(r-R_o)^2 \left(\frac{d^2V}{dr^2}\right)_{R_o} \right] P_{nl}(r)$$

Assuming that the vibrational motion produces only small displacements… $r \approx R_o$

$$\frac{\hbar^2 l(l+1)}{2\mu r^2} \approx \frac{\hbar^2 l(l+1)}{2\mu R_o^2}$$

$$\boxed{E_{\mathrm{r}}^{nl} = V_o + \hbar\omega_o(n + \frac{1}{2}) + \frac{\hbar^2 l(l+1)}{2\mu R_o^2}}$$

Divide and Conquer



$$\Psi(\mathbf{r}, \mathbf{R_1}, \mathbf{R_2})$$

$$\Phi(\mathbf{R_1}, \mathbf{R_2})\psi(\mathbf{r}; \mathbf{R_1}, \mathbf{R_2})$$

$$F(\mathbf{R})\phi_{\mathbf{nlm}}(\mathbf{r}, \theta, \phi)$$

$$C\,[\phi_1 + \phi_2]$$

$$\frac{P_{nl}(r)}{r} Y_{lm}(\theta, \phi)$$

Approximations

- Born-Oppenheimer
  - Nuclei inside electron cloud act as if they are embedded in an elastic medium (V_{eff})
- Effective potential (V_{eff}) is parabolic
  - Vibrations of simple harmonic oscillator
- Rigid rotor
  - Vibrations only displace nuclei slightly from equilibrium bond length

Total Energy of the H_2 Molecule

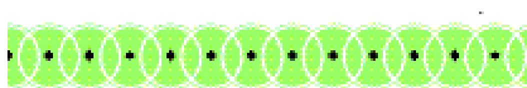
$$E = E_{n\ell mK} = E_{\mathbf{r}} + E_{\mathbf{R}}$$

$$E_{n\ell mK} = \underbrace{V_o}_{\text{Binding}} + \underbrace{\hbar\omega_o(n + \frac{1}{2})}_{\text{Vibrational}} + \underbrace{\frac{\hbar^2 l(l+1)}{2\mu R_o^2}}_{\text{Rotational}} + \underbrace{\frac{\hbar^2|\mathbf{K}|^2}{2M}}_{\text{Translational}}$$

	Binding	Vibrational	Rotational	Translational
H_2	1.4 eV	0.5 (n + ½) eV	7.5 l (l+1) meV	
O_2	1.0 eV	0.1 (n + ½) eV	30 l (l +1) meV	
	30 THz	3-30 THz	0.3-3 THz	

Generalizations from Molecules to Solids

- The source of the binding energy is primarily the electrostatic potential between the nuclei and the electrons. The localization energy can also play a role (metal).
- Nuclear motions of the ions contribute a very small part to the binding energy.
- Sharing electrons between nuclei lowers the energy of the solid.
- The potential between the nuclei is of the same form as the molecule.
- Exicted states exists.



Assumptions for Electronic States

- One electron energy levels
- No spin or exchange energies
- LCAO a good approximation
- Ignore motion of the nuclei to first order