

Quantum Mechanics II

Quantum Physics of Few-Body Systems

**Molecular Forces and Stability;
Molecular Spectra**

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Few-Body Systems

Molecular Forces

- The Güttinger('32)-Pauli('33)-Hellmann('37)-Feynman('39) Theorem:

$$\hat{H} = \hat{H}(\lambda) \quad E = E(\lambda)$$

$$\frac{\partial E(\lambda)}{\partial \lambda} := \frac{\partial \langle \hat{H}(\lambda) \rangle}{\partial \lambda} \stackrel{!}{=} \left\langle \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle$$

- This permits:

- re-introducing the notion of force.
- Consider a diatomic molecule (*a* fixed, *b* movable)

$$\hat{H} = -\vec{\nabla}^2 + \frac{2}{R} - \frac{2}{r_a} - \frac{2}{r_b}$$

- The rate of change of energy w.r.t. varying *R* is:

$$-\frac{\partial E}{\partial R} = \left\langle \frac{\partial}{\partial R} \left[\frac{2}{R} - \frac{2}{r_a} - \frac{2}{r_b} \right] \right\rangle = \frac{2}{R^2} + \int d^3\vec{r}_b \frac{\partial}{\partial R} \left[\frac{2}{r_a} + \frac{2}{r_b} \right] |\psi_e|^2$$

“*a*” is fixed!

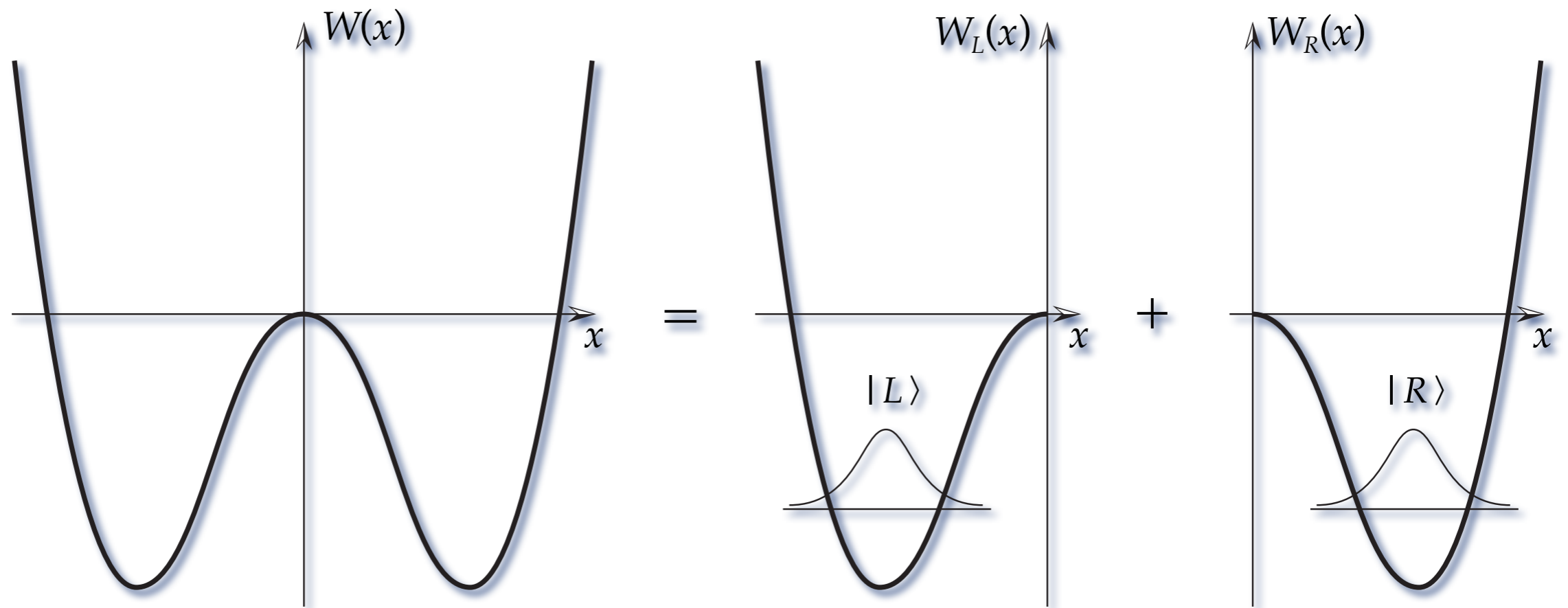
$$\frac{\partial}{\partial R} \left[\frac{2}{r_a} + \frac{2}{r_b} \right] = \left[\frac{\partial}{\partial R} \frac{2}{r_b} \right] = \frac{\vec{R}}{R} \cdot \left[\vec{\nabla} \frac{1}{r_b} \right] = -\frac{\vec{R} \cdot \vec{r}_b}{R r_b^3} \quad \text{restoring force}$$

Conceptually useful!

Few-Body Systems

Molecular Forces

- Toy model: a double potential well



- Approximating that the two wells are far from each other

$$i\hbar \frac{\partial}{\partial t} |L\rangle = \left[-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + W_L \right] |L\rangle$$

$$i\hbar \frac{\partial}{\partial t} |R\rangle = \left[-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + W_R \right] |R\rangle$$

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \left[-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + W_L + W_R \right] |\psi\rangle$$

Few-Body Systems

Molecular Forces

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \left[-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + W_L + W_R \right] |\psi\rangle$$

Look for solutions $|\psi\rangle = a_L(t) |L\rangle + a_R(t) |R\rangle$

$$\begin{aligned} i\hbar \left[\dot{a}_L |L\rangle + \dot{a}_R |R\rangle + a_L \left(-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + W_L \right) |L\rangle + a_R \left(-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + W_R \right) |R\rangle \right] \\ = \left[-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + W_L + W_R \right] a_L |L\rangle + \left[-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + W_L + W_R \right] a_R |R\rangle \end{aligned}$$

so...

$$i\hbar \left[\dot{a}_L |L\rangle + \dot{a}_R |R\rangle \right] = W_R a_L |L\rangle + W_L a_R |R\rangle$$

Now project, recalling that $\alpha := \langle L|R\rangle \neq 0$

$$\langle L| : i\hbar (\dot{a}_L + \alpha \dot{a}_R) = U a_L + V a_R \quad U := \langle L|W_R|L\rangle = \langle R|W_L|R\rangle$$

$$\langle R| : i\hbar (\alpha \dot{a}_L + \dot{a}_R) = V a_L + U a_R \quad V := \langle R|W_R|L\rangle = \langle L|W_L|R\rangle$$

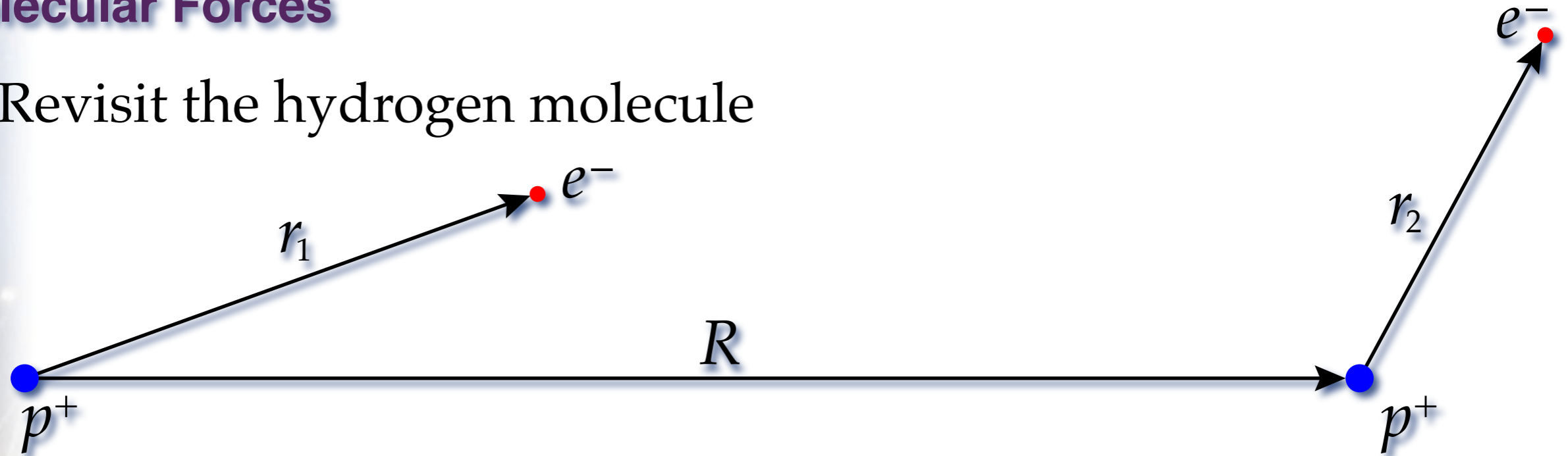
writing $a_L(t) = A_L e^{-i\omega t}$ $a_R(t) = A_R e^{-i\omega t}$

$$\hbar\omega_{\pm} = \frac{U \pm V}{1 \pm \alpha} \xrightarrow[\alpha \ll 1]{V \ll U} U \dots \text{the two states, symmetric and antisymmetric; one shifted down, the other up ...in agreement with the earlier results.}$$

Few-Body Systems

Molecular Forces

- Revisit the hydrogen molecule



- Add the potentials just as in classical physics:

- P.E. of atom 2 w.r.t. proton 1 (to 1st order)

$$W(\vec{R}, \vec{r}_2) = \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\vec{R}|} - \frac{1}{|\vec{R} + \vec{r}_2|} \right] \approx -\frac{e^2}{4\pi\epsilon_0} (\vec{r}_2 \cdot \vec{\nabla}_{\vec{R}}) \frac{1}{|\vec{R}|}$$

- P.E. of atom 2 w.r.t. atom 1 (incl. the 1st electron)

$$W(\vec{R}, \vec{r}_2) - W(\vec{R} - \vec{r}_1, \vec{r}_2) \approx -\frac{e^2}{4\pi\epsilon_0} (\vec{r}_1 \cdot \vec{\nabla}_{\vec{R}}) (\vec{r}_2 \cdot \vec{\nabla}_{\vec{R}}) \frac{1}{|\vec{R}|} =: \hat{H}'$$

- Choose the z-axis along the protons...

$$\hat{H}' = \frac{e^2}{4\pi\epsilon_0 R^3} [(\vec{r}_1 \cdot \vec{r}_2) - 3z_1 z_2] = \frac{e^2}{4\pi\epsilon_0 R^3} [x_1 x_2 + y_1 y_2 - 2z_1 z_2]$$

Few-Body Systems

Molecular Forces

- In Rydberg-Bohr radius units,

$$\hat{H} = -\vec{\nabla}_1^2 - \vec{\nabla}_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{R^3} [x_1x_2 + y_1y_2 - 2z_1z_2]$$

$$\psi^{(0)} = \frac{1}{\pi} e^{-(r_1+r_2)}$$

- Deform this trial wave-function:

$$\psi = \frac{N}{\pi} \left[1 - \frac{1}{R^3} (x_1x_2 + y_1y_2 - 2z_1z_2) \right] e^{-(r_1+r_2)}$$

- Keeping consistently only the two leading orders of R ,

- Normalization: $N \approx \sqrt{1 - \frac{3}{R^3}}$

- Total energy: $E \approx -2 \left(1 + \frac{6}{R^6} \right)$

- More careful variational estimates turn the coeff. into 6.4990...

- Prediction of the typical $\sim R^{-6}$ molecular potential

- ...and then R^{-12} , etc.

Few-Body Systems

Molecular Spectra

- Hydrogen atom:

$$\begin{aligned}
 E_n^{(0)} &= -\frac{1}{n^2} \text{Ry} = -\frac{1}{n^2} \frac{M_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} = -\frac{1}{n^2} \frac{\hbar^2}{2M_e} \left(\frac{M_e e}{(4\pi\epsilon_0)\hbar} \right)^2 \\
 &= -\frac{1}{n^2} \frac{\hbar^2}{2M_e a_0^2}
 \end{aligned}$$

- Particle in an infinite potential well of width a :

$$\begin{aligned}
 E_n &= n^2 \frac{\pi^2 \hbar^2}{2Ma^2} \\
 \Delta E &\sim \frac{(\Delta p)^2}{2M} \sim \frac{1}{2M} \left(\frac{\hbar}{2\Delta x} \right)^2 = \frac{1}{2M} \left(\frac{\hbar}{2(a/2)} \right)^2 = \frac{\hbar^2}{2Ma^2}
 \end{aligned}$$

- The electron energy in a diatomic molecule (size $\sim L_m$)

$$E_e \sim \frac{\hbar^2}{M_e L_m^2}$$

- Excited states need not be bound (H_2^+)
- If more than just the ground state, expect an n^γ -spectrum ($-2 \leq \gamma \leq 2$)

Few-Body Systems

Molecular Spectra

$$E_e \sim \frac{\hbar}{M_e L_m^2}$$

- Diatomic molecules can vibrate (R -oscillations)

$$E_v = \hbar\omega\left(n + \frac{1}{2}\right) = \hbar\sqrt{\frac{K}{\mu_m}}\left(n + \frac{1}{2}\right)$$

- Stretching the molecule to L_m strains its (electronic) binding:

$$\frac{1}{2}K L_m^2 \sim E_e \Rightarrow K \sim \frac{E_e}{L_m^2} \sim \frac{M_e E_e^2}{\hbar^2} \Leftarrow \frac{1}{L_m^2} \sim \frac{M_e E_e}{\hbar^2}$$

$$\omega = \sqrt{\frac{K}{\mu_m}} \sim \sqrt{\frac{M_e E_e^2}{\mu_m \hbar^2}} \sim \sqrt{\frac{M_e}{\mu_m}} \frac{E_e}{\hbar}$$

- So,

$$E_v = \hbar\omega\left(n + \frac{1}{2}\right) \sim \sqrt{\frac{M_e}{\mu_m}}\left(n + \frac{1}{2}\right)E_e$$

- Note: μ_m is the reduced molecular mass

- For example, for H_2 , $\mu_m = \frac{1}{2}M_p$ $\sqrt{M_e/\mu_{H_2}} \approx \frac{1}{30}$

- Typically, $\mu_m \gg M_e$ in all molecules, by $10^3 - 10^4$

Few-Body Systems

Molecular Spectra

- Diatomic molecules can also rotate

- About the $p^+ - p^+$ axis ...small moment of inertia, too much energy

- About the two axes perpendicular to the $p^+ - p^+$ axis

$$E_r = \frac{\mathcal{L}^2}{2I} \sim \frac{\hbar^2 \ell(\ell+1)}{2(\mu_m L_m^2)} = \frac{M_e}{\mu_m} \ell(\ell+1) \frac{\hbar^2}{2M_e L_m^2} = \frac{M_e}{\mu_m} \ell(\ell+1) E_e$$

- Comparing the electronic *vs.* vibrational *vs.* rotational energy

$$E_e : E_v : E_r \sim 1 : \sqrt{\frac{M_e}{\mu_m}} : \frac{M_e}{\mu_m} \approx 1 : \frac{1}{30} : \frac{1}{900}$$

- For example, the 2nd $1/30$ ratio is in fact close to $1/79$ for HCl

- Besides these rough estimates

“order-of-magnitude
(ball-park) estimates”

- ...this neglects that rotation stretches L_m

- ...and so affects vibrations and the electronic energy

- ...this approximates the $\sim R^{-6} + \dots$ vibrational potential w/ LHO

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*Now, go forth and
calculate!!!*

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