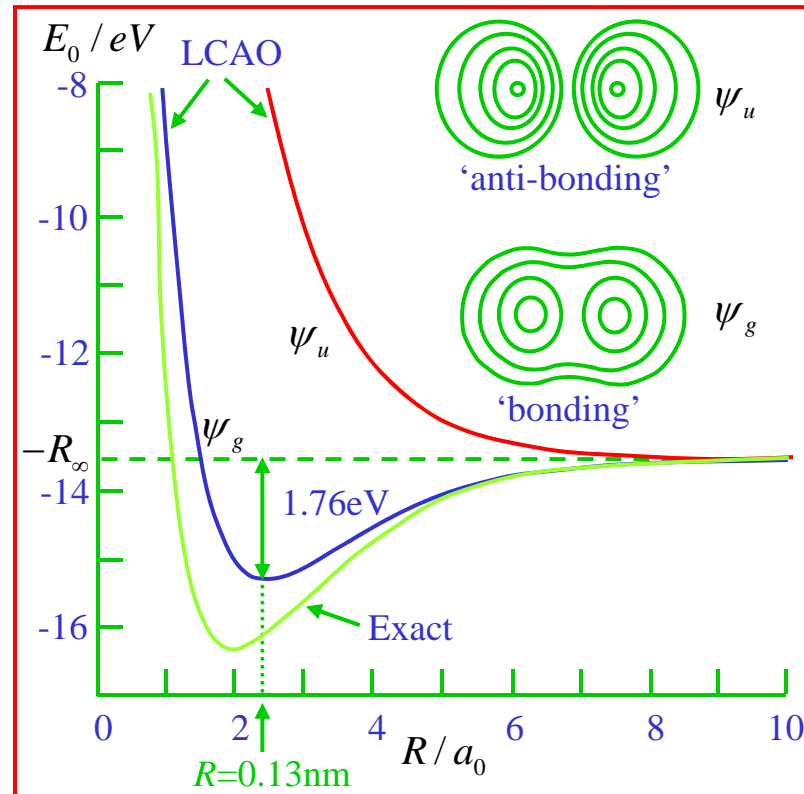


Advanced Quantum Physics

Lecture 6



David Ritchie

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Section 2 –Methods of Approximation

- Very few problems in Quantum Mechanics can be solved analytically.
- For many situations we must resort to approximate techniques.



- 2.1 Variational method
- 2.2 Born-Oppenheimer approximation
- 2.3 Time-independent Perturbation theory
- 2.4 Degenerate Perturbation theory

Hydrogen atom (1) – Revision

- The hydrogen atom allows for very precise tests of quantum theory.
- In QP section 8.9 Schrodinger's equation was solved for hydrogen.
- Solutions are of the form: $R(r)Y_{l,m}(\theta, \phi)$ and solving the radial equation introduces a radial quantum number $n_r \geq 0$.
- For a Coulomb potential, the energy depends on a principal quantum number $n = n_r + l + 1 \geq 1$ and not on l and n_r separately.
- The energy levels are $E_n = -R_\infty / n^2$ where the Rydberg constant (binding energy of ground-state hydrogen atom) is defined by:

$$R_\infty = \frac{\mu e^4}{2(4\pi\epsilon_0)^2 \hbar^2} = \frac{e^2}{8\pi\epsilon_0 a_0} = \frac{1}{2} \mu c^2 \alpha^2 \approx 13.6 eV$$

- In this definition the reduced mass, μ is given by: $\mu = m_e \left(1 + \frac{m_e}{m_N}\right)^{-1}$ with m_N being the nuclear mass. The Bohr radius a_0 and fine structure constant α definitions are now:

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} \approx 0.529 \times 10^{-10} m, \quad \alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$$

- We introduce the conventional notation where values of $l = 0, 1, 2, 3, 4, \dots$

Are represented by letters s, p, d, f, g, ...

Hydrogen atom (2)

- Since $n \geq 1$ and $n_r \geq 0$ the allowed combinations of quantum numbers are:

n	l	Subshells
1	0	1s
2	0,1	2s 2p
3	0,1,2	3s 3p 3d
4	0,1,2,3	4s 4p 4d 4f
n	0...(n-1)	ns...

- $E_n = -R_\infty/n^2$ implies, for example, exact degeneracy of the 2s and 2p, and of the 3s, 3p and 3d levels.
- This theory also applies to other single electron systems e.g. He⁺, Li⁺⁺.
- Nuclear charge Z , Bohr radius reduced by $\frac{1}{Z}$ energy $E_n = -Z^2 R_\infty/n^2$
- For multielectron atoms screening plays an important role, the Coulomb potential is no longer $\frac{1}{r}$ - the degeneracy between 2s and 2p or 3s,3p and 3d is broken.

Hydrogen atom (3)

•The radial wavefunctions for H atom are: $R_{nl}(r)$

•The radial probability distribution functions are: $r^2 R_{nl}^2(r)$

$$n = n_r + \ell + 1 \geq 1$$

•The form of radial distribution is determined by the value of n_r .

$$\psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0}$$

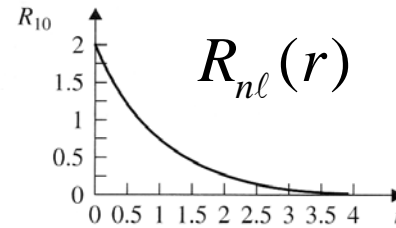
$$\psi_{2s} = \sqrt{\frac{1}{8\pi a_0^3}} (1 - r/2a_0) e^{-r/2a_0}$$

$$\psi_{2p_0} = \sqrt{\frac{1}{32\pi a_0^5}} r e^{-r/2a_0} \cos \theta$$

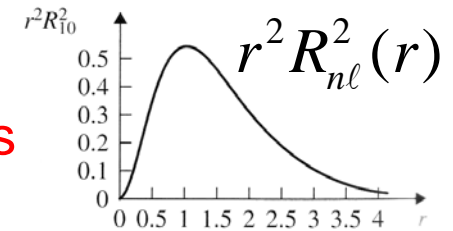
$$\psi_{2p_{\pm 1}} = \sqrt{\frac{1}{64\pi a_0^5}} r e^{-r/2a_0} \sin \theta e^{\pm i\phi}$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m}$$

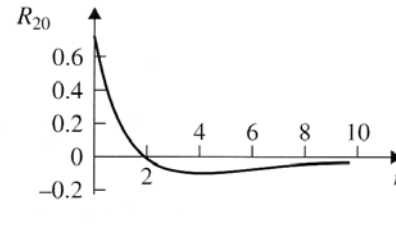
$n = 1$
 $\ell = 0$
 $n_r = 0$



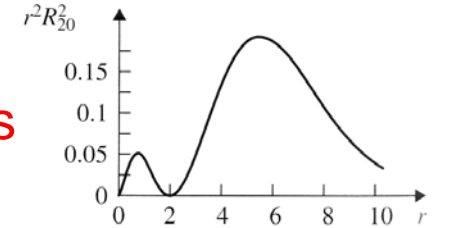
1s



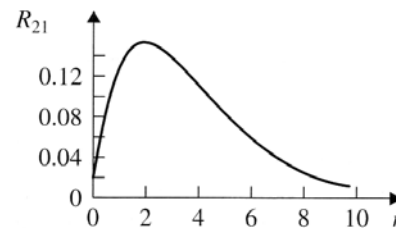
$n = 2$
 $\ell = 0$
 $n_r = 1$



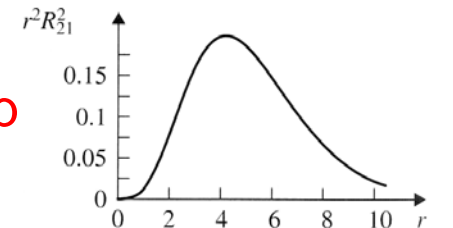
2s



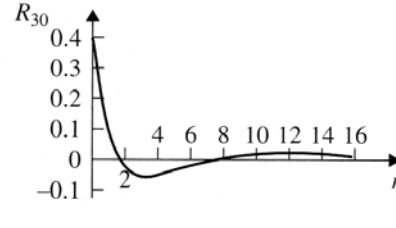
$n = 2$
 $\ell = 1$
 $n_r = 0$



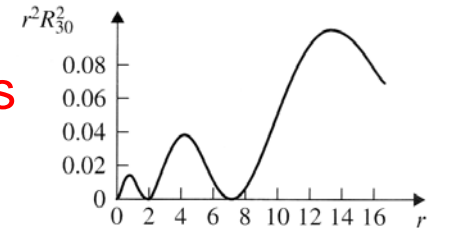
2p



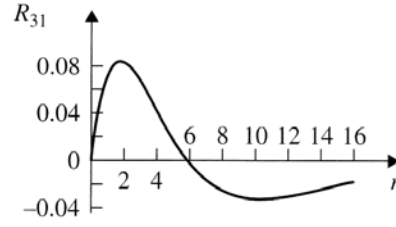
$n = 3$
 $\ell = 0$
 $n_r = 2$



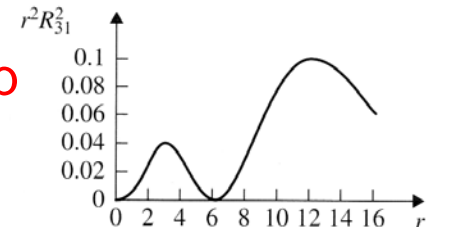
3s



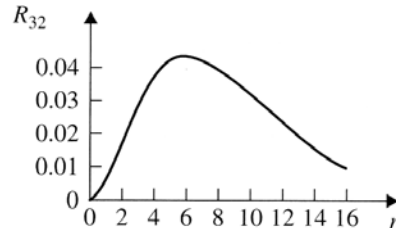
$n = 3$
 $\ell = 1$
 $n_r = 1$



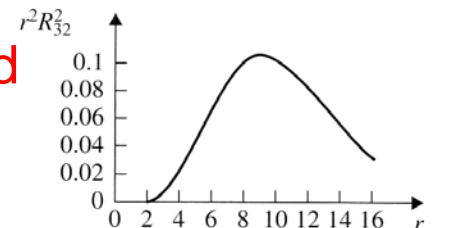
3p



$n = 3$
 $\ell = 2$
 $n_r = 0$



3d



Hydrogen atom (4)

- The angular part of the H atom wavefunction is formed by spherical harmonics $Y_{lm}(\theta, \phi)$.
- $|Y_{lm}(\theta, \phi)|^2$ shown in picture:
- Their shape varies with different values of l and m .

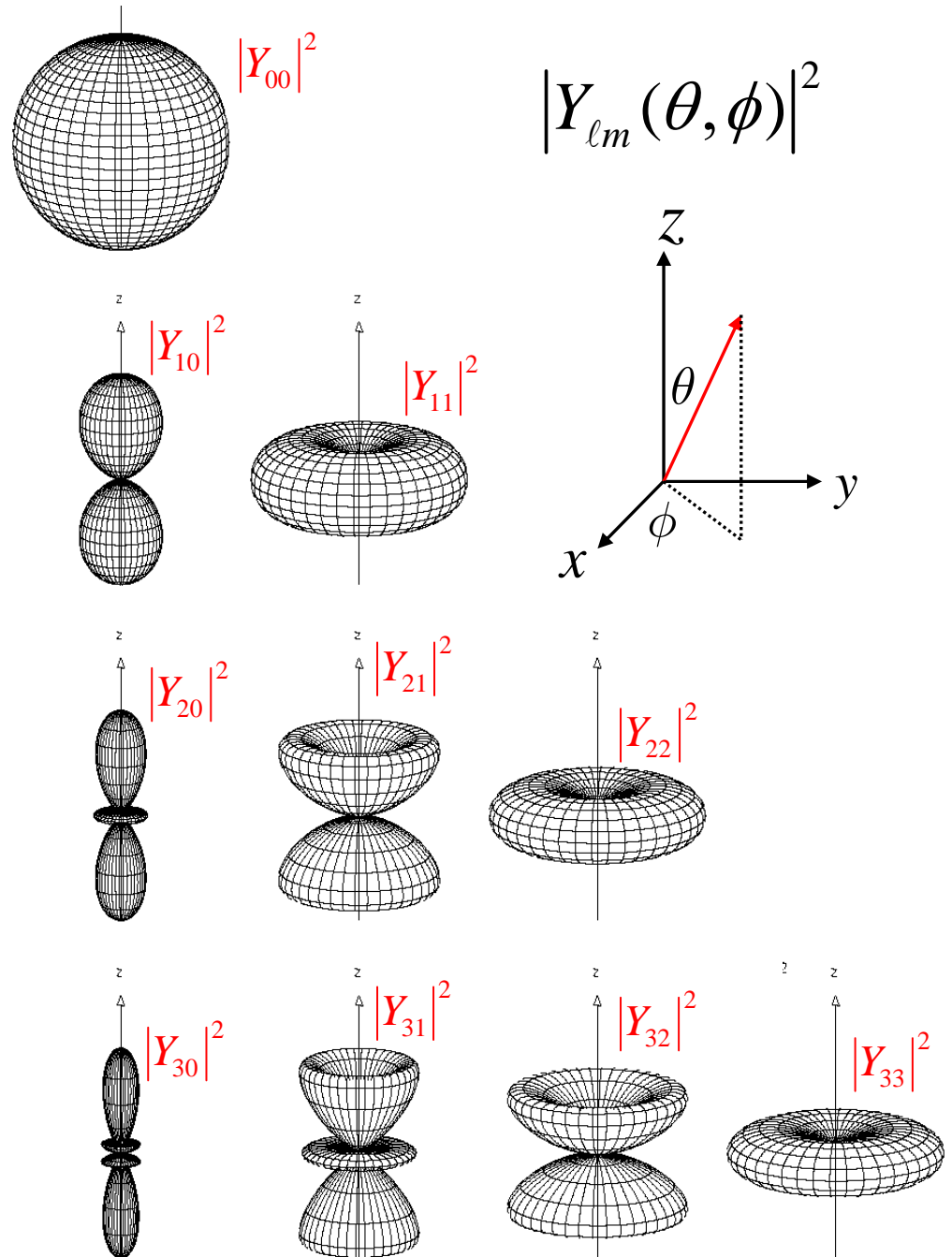
$$\psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0}$$

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$$\psi_{2p_{\pm 1}} = \sqrt{\frac{1}{64\pi a_0^5}} r e^{-r/2a_0} \sin \theta e^{\pm i\phi}$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} m$$



The Born-Oppenheimer approximation (1)

- A molecule consists of electrons – $n=1,2,3..$ And nuclei – $N=a,b,c...$ moving in a potential set up by all the electric charges.
- Even in Classical physics this is a difficult problem...
- Fortunately because nuclei have a much greater mass ($>10^3$) than the electrons, we can treat the electrons and nuclei separately.
- The forces on nuclei are similar to those on electrons implying that comparable momenta are imparted to both by their interactions.
- Hence nuclei moving much more slowly than electrons.
- To study the electron motion we treat nuclei as being in fixed positions.
- To study nuclear motion (vibrations and rotation of molecule) we assume electrons adjust instantly to changes in positions of nuclei.
- These assumptions form the basis of the *Born-Oppenheimer approximation*.

The Born-Oppenheimer approximation (2)

- In QM the wavefunction of the molecule, $\Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}, t)$ is a function of the positions of electrons \mathbf{r}_n and nuclei \mathbf{R}_N

- Hamiltonian is of a form:
$$\hat{H} = \sum_{n=1,2,\dots} \frac{\hat{\mathbf{p}}_n^2}{2m_e} + \sum_{N=a,b,\dots} \frac{\hat{\mathbf{p}}_N^2}{2m_N} + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$$

where $\hat{\mathbf{p}}_n$ and $\hat{\mathbf{p}}_N$ act only on corresponding coordinates, e.g.:

$$\hat{\mathbf{p}}_a^2 \Psi = -\hbar^2 \nabla_a^2 \Psi = -\hbar^2 \left(\frac{\partial^2 \Psi}{\partial x_a^2} + \frac{\partial^2 \Psi}{\partial y_a^2} + \frac{\partial^2 \Psi}{\partial z_a^2} \right)$$

- Comparable momenta for electrons & nuclei implies $\nabla_n^2 \Psi$ and $\nabla_N^2 \Psi$ similar.

- We can neglect nuclear KE term in Hamiltonian above since $m_N \gg m_e$.

- In the Born - Oppenheimer approx. the Schrodinger equation is:

$$\left[\frac{-\hbar^2}{2m_e} \sum_{n=1,2,\dots} \nabla_n^2 + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) \right] \psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) = E_k(\{\mathbf{R}_N\}) \psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$$

- As *molecular conformation* is varied by changing nuclear positions $\mathbf{R}_a, \mathbf{R}_b, \dots$ ground state energy E_0 can be minimised to find *equilibrium conformation*.

The H₂⁺ ion

- Simplest molecule – two protons (at $\mathbf{R}_a, \mathbf{R}_b$) & one electron (at \mathbf{r})
- Schrodinger's equation:

$$\left\{ \frac{-\hbar^2}{2m_e} \nabla_r^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\mathbf{R}_a - \mathbf{R}_b|} - \frac{1}{|\mathbf{r} - \mathbf{R}_a|} - \frac{1}{|\mathbf{r} - \mathbf{R}_b|} \right] \right\} \psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b) = E\psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b)$$

- Solved exactly with elliptical polars, but for fun we use Variational Method.
- Trial electron wavefunction - linear combination of ground state atomic wavefunctions centred on two protons:

$$\psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b) = \alpha\psi_a + \beta\psi_b \quad \text{where} \quad \psi_{a,b} = (\pi a_0^3)^{-\frac{1}{2}} \exp(-|\mathbf{r} - \mathbf{R}_{a,b}|/a_0)$$

- $a_0 = 53\text{pm}$ is the Bohr radius, we take parameters α and β to be real.
- The expression to be minimised is:

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle \alpha\psi_a + \beta\psi_b | \hat{H} | \alpha\psi_a + \beta\psi_b \rangle}{\langle \alpha\psi_a + \beta\psi_b | \alpha\psi_a + \beta\psi_b \rangle} = \frac{\alpha^2 H_{aa} + \beta^2 H_{bb} + 2\alpha\beta H_{ab}}{\alpha^2 + \beta^2 + 2\alpha\beta S}$$

- Where, by symmetry

$$H_{aa} = \langle \psi_a | \hat{H} | \psi_a \rangle = H_{bb} = \langle \psi_b | \hat{H} | \psi_b \rangle, \quad H_{ab} = \langle \psi_a | \hat{H} | \psi_b \rangle = \langle \psi_b | \hat{H} | \psi_a \rangle$$

$$\text{and } S = \langle \psi_a | \psi_b \rangle$$

The H₂⁺ ion (2)

- Because ψ_a and ψ_b are not orthogonal we introduce the overlap integral between the two atomic wavefunctions $S = \langle \psi_a | \psi_b \rangle$.
- This can be simplified further – because potential is symmetric about mid-point between protons, wavefunction is symmetric or antisymmetric.

- So $\alpha = \pm\beta$ and hence,

$$\langle E \rangle = \frac{\alpha^2 H_{aa} + \beta^2 H_{bb} + 2\alpha\beta H_{ab}}{\alpha^2 + \beta^2 + 2\alpha\beta S} = \frac{H_{aa} \pm H_{ab}}{1 \pm S} \geq E_0$$

- Integrals tedious – results are:

$$S = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right) e^{-R/a_0}, \quad H_{aa} = -R_\infty + \frac{e^2}{4\pi\epsilon_0 R} \left(1 + \frac{R}{a_0} \right) e^{-2R/a_0}$$

$$H_{ab} = \frac{e^2}{4\pi\epsilon_0 a_0} \left(1 + \frac{R}{a_0} \right) e^{-R/a_0} + S \left(-R_\infty + \frac{e^2}{4\pi\epsilon_0 R} \right)$$

where $R = |\mathbf{R}_a - \mathbf{R}_b|$ and R_∞ is the Rydberg constant (the binding energy of the ground-state H atom).

The H₂⁺ ion (3)

- We have two possible wavefunctions for the H₂⁺ ion:

$$\psi_g = (\psi_a + \psi_b) / \sqrt{2(1+S)} \quad ; \quad \psi_u = (\psi_a - \psi_b) / \sqrt{2(1-S)}$$

- Where the normalization factors are given by

$$1 / \sqrt{\langle \psi_a \pm \psi_b | \psi_a \pm \psi_b \rangle} = 1 / \sqrt{(2 \pm 2S)}$$

- With energies:

$$E_g = (H_{aa} + H_{ab}) / (1+S) \quad ; \quad E_u = (H_{aa} - H_{ab}) / (1-S)$$

- Subscript *g* (from *gerade* – German for even) means the state is even when electron wavefunction is inverted around centre of symmetry of molecule i.e. :

$$\mathbf{r} \rightarrow \mathbf{R}_a + \mathbf{R}_b - \mathbf{r}$$

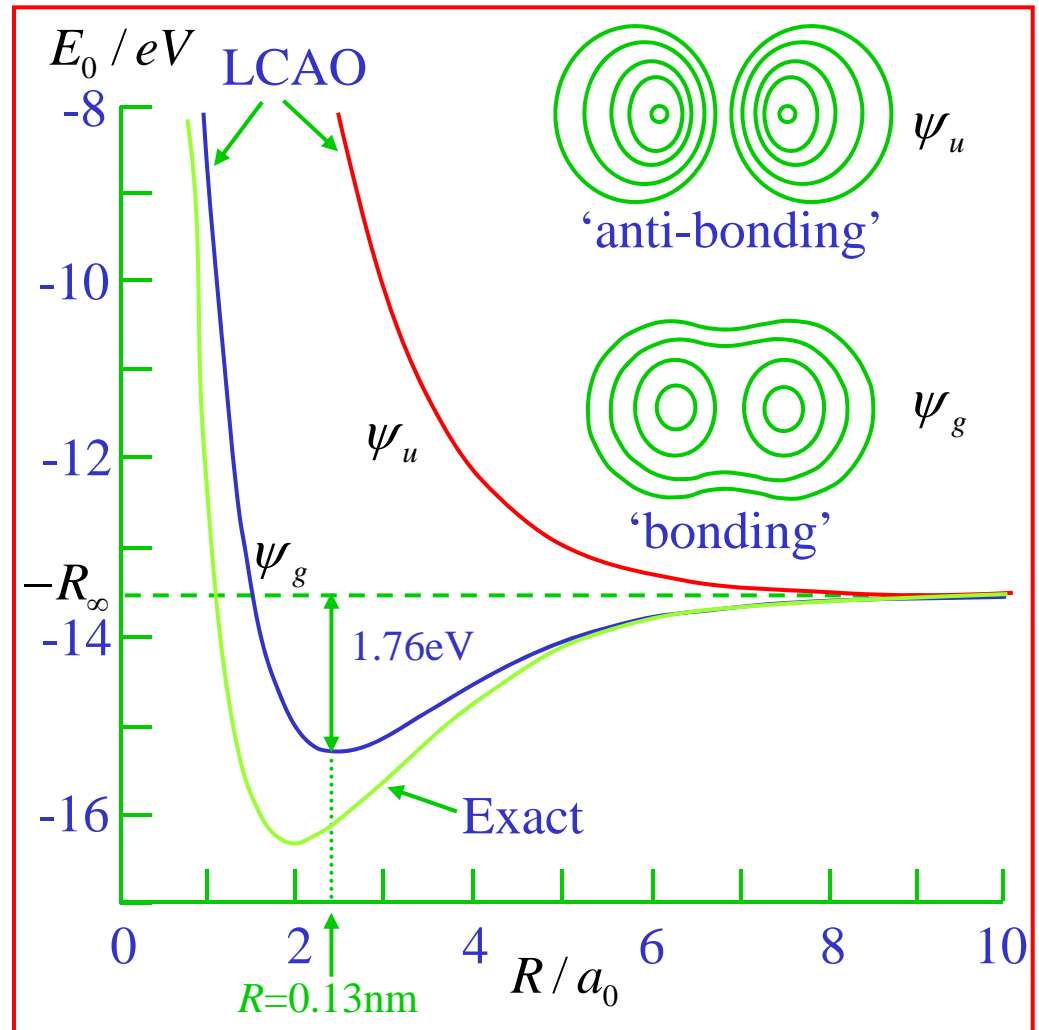
- This interchanges ψ_a and ψ_b and is *not* the same as parity inversion which also affects nuclear coordinates.

- Subscript *u* denotes *ungerade* (odd) state.

- Note that ψ_g and ψ_u are orthonormal, they *diagonalize* the Hamiltonian, in chemistry they are known as *molecular orbitals* and this approach is called the *linear combination of atomic orbitals* (LCAO) approximation.

The H_2^+ ion (4)

- LCAO approx gives $E_0 \rightarrow -R_\infty$ as $R \rightarrow \infty$ - as expected.
- State ψ_g lower energy than ψ_u , minimum energy at $R=0.13\text{nm}$ and molecular binding energy of 1.76eV .
- In ψ_g the two atomic wave-functions interfere constructively - enhanced electron density between the protons screening the proton's electric field.
- In contrast ψ_u has destructive interference, greater p-p repulsion - not a bound state.
- Variational method gives upper bound on ground state – true potential energy lies below LCAO.
- True dissociation energy 2.8eV , equilibrium separation 106pm .



- Failed at small R – improve by using more atomic orbitals, allowing variable effective nuclear charge (screening) etc.

Labelling of molecular orbitals

- Helpful to introduce notation to label molecular orbitals.
- We have used linear combinations of atomic wavefunctions which themselves have no orbital angular momentum.
- However these linear combinations are not isotropic ('dumbbell' shape).
- Molecular wavefunction does not have unique electronic orbital angular momentum since $\hat{\mathbf{L}}^2$ for electron does not commute with \hat{H} because of non-central $1/|\mathbf{r} - \mathbf{R}_a|$, $1/|\mathbf{r} - \mathbf{R}_b|$ terms in potential.
- Only component of $\hat{\mathbf{L}}$ that commutes is \hat{L}_z : z -axis chosen parallel to internuclear axis $\mathbf{R}_a - \mathbf{R}_b$.
- Instead of classifying states as s-, p-, d-, ... Orbitals ($l=0,1,2,3,\dots$) we call them σ -, π -, δ -... according to whether $\Lambda = 0,1,2,\dots$ where $\Lambda \equiv |m_\ell|$
- Subscript g or u denotes if state is even or odd under inversion.
- Notation applied to homonuclear diatomic molecules - symmetric potential
- Ground state of H_2^+ ion σ_g corresponding odd state σ_u^* (* antibonding)
- In LCAO approx. molecular orbitals written as $1s\sigma_g$ and $1s\sigma_u^*$

The H₂ Molecule

- Not a trivial extension of H₂⁺ ion.
- For two electrons at $\mathbf{r}_{1,2}$, two protons at $\mathbf{R}_{a,b}$ Hamiltonian:

$$-\frac{\hbar^2}{2m_e}(\nabla_{r_1}^2 + \nabla_{r_2}^2) + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} \right]$$

where $r_{1b} = |\mathbf{r}_1 - \mathbf{R}_b|$ etc. Sum of two Hamiltonians for H₂⁺, plus additional term:

$$\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} - \frac{1}{r_{ab}} \right)$$

- Expectation values of $1/r_{12}$ & $1/r_{ab}$ probably quite similar – treat term as perturbation.
- So as first approx. neglect this term, assign each electron to one of the H₂⁺ molecular orbitals defined above. Four ways of filling two orbitals σ_g & σ_u^* :

$$\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2), \quad \psi_g(\mathbf{r}_1)\psi_u^*(\mathbf{r}_2), \quad \psi_u^*(\mathbf{r}_1)\psi_g(\mathbf{r}_2), \quad \psi_u^*(\mathbf{r}_1)\psi_u^*(\mathbf{r}_2)$$

- The first should be the ground state...
- The electrons are identical Fermions – antisymmetric wavefunction – so two electrons in same spatial state must be in singlet spin state.

The H₂ Molecule (2)

- Two electron in symmetric ground state $\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2)$ must be in anti-symmetric singlet spin state:

$$X_{0,0} = [\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)]/\sqrt{2}$$

- Here ground state electrons spin paired to give zero resultant – both electrons in σ_g ‘bonding’ orbital – enhanced electron density between protons.
- Calculation of energy of this state as function of nuclear separation is a minimum at $R = R_0 = 85\text{pm}$ - with a binding energy of 2.7eV .

- The true molecule is smaller and more tightly bound than this.

- Using a variable effective charge:

- allows variation in atomic orbitals & gives value of R_0 much closer to experiment but the binding energy still too low. Reason: σ_g^2 is not a good representation of the ground state.

Approximation	BE/eV	R/pm
Experiment	4.75	74.1
MO fixed charge	2.70	85.2
MO variable charge	3.49	73.0
VB variable charge	3.78	74.6
Variable λ and charge	4.03	75.7
13 variable parameters	4.72	74.1

The H₂ Molecule (3)

- Multiplying out spatial part of σ_g^2 wavefunction in LCAO approx we get:

$$\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2) \propto [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] + [\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_b(\mathbf{r}_2)]$$

- First bracket - electrons being shared between H atoms – *covalent bonding*
- Second bracket, both electrons assigned to same atom – *ionic bonding*.
- Equation suggests ionic and covalent contributions are the same - implies that if we split the molecule we are equally likely to get H⁺ and H⁻ ions as we are to get to two H atoms – however this is unlikely due to e-e repulsion.
- If we drop ionic part – ‘Valance band approx’ – binding energy and R_0 improved

- Including λ parameter for ionic part:

$$\psi^{VB} \propto [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] + \lambda[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_b(\mathbf{r}_2)]$$

- Optimal value $\lambda = 1/6$ - 2.7% probability of ionic configuration – still not good.

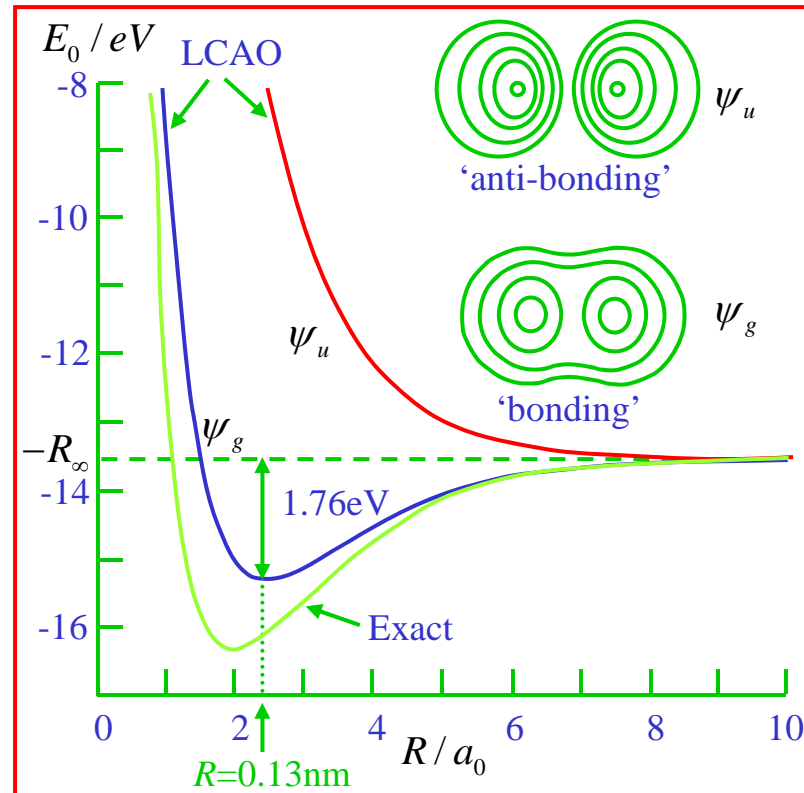
- But with enough (13) free parameters we get excellent agreement...!!

Approximation	BE/eV	R/pm
Experiment	4.75	74.1
MO fixed charge	2.70	85.2
MO variable charge	3.49	73.0
VB variable charge	3.78	74.6
Variable λ and charge	4.03	75.7
13 variable parameters	4.72	74.1

Lecture 6 - Summary

- Revision of hydrogen atom energy levels and wavefunctions.
- Molecules – the Born-Oppenheimer approximation. To study electron motion we assume that nuclei are in *fixed* positions. To study nuclear motion we assume electrons adjust *instantly* to changes in the positions of nuclei.
- The H_2^+ ion – use of a linear combination of atomic orbitals (LCAO) to form bonding and anti-bonding *molecular orbitals*. Calculation of nuclear separation and binding energy.
- The H_2 molecule – use of H_2^+ *molecular orbitals* and variable parameters to calculate nuclear separation and binding energy. Splitting of wavefunction into *covalent* and *ionic* parts.

Lecture 6



The End!!

(www.sp.phy.cam.ac.uk/~dar11/pdf)