Electron States of Diatomic Molecules

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The hamiltonian for a diatomic molecule can be considered to be made up of three terms

$$\hat{H} = \hat{T}_N + \hat{T}_{el} + \hat{V}$$

where $\hat{T}_N$ is the kinetic energy operator for nuclear motion, $\hat{T}_{el}$ is the kinetic energy operator for the electronic motion and $\hat{V}$ is operator comprising all electrostatic interactions

$$\hat{V} = -\sum_i \frac{1}{|\vec{r}_i - \vec{R}/2|} - \sum_i \frac{1}{|\vec{r}_i + \vec{R}/2|} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \frac{1}{R}$$

Hamiltonian for a Diatomic Molecule

In the explicit form, the Hamiltonian is

$$\hat{H} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_N \frac{1}{2M_N}\nabla_N^2 - \sum_i \frac{Z_A}{|\vec{r_i} - \vec{r_A}|} - \sum_i \frac{Z_B}{|\vec{r_i} - \vec{r_B}|} + \sum_i \sum_{j>i} \frac{1}{|\vec{r_{ij}}|} + \frac{Z_A Z_B}{|\vec{r_{AB}}|}$$

where $\vec{r_i}$ is the position of the ith electron w.r.t. the center-of-mass, and $\vec{r_A}$ and $\vec{r_B}$ are the positions of the nuclei.

It is usual to make the abbreviations $\vec{R} = \vec{r_A} - \vec{r_B}$ and $\vec{r_{ij}} = \vec{r_i} - \vec{r_j}$ etc.

For a homonuclear diatomic $\vec{r_A} = \frac{1}{2}\vec{R}$ and $\vec{r_B} = -\frac{1}{2}\vec{R}$, and $Z_A = Z_B = Z$, so that the hamiltonian becomes

$$\hat{H} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_N \frac{1}{2M_N}\nabla_N^2 - \sum_i \frac{Z}{|\vec{r_i} - \vec{R}/2|} - \sum_i \frac{Z}{|\vec{r_i} + \vec{R}/2|} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \frac{Z^2}{R}$$

Comparison of Nuclear and Electronic Motions

- The motion of the centre-of-mass is unimportant, since we are only interested in internal motion of the nuclei and electrons, not in the overall translational motion
- Since there are only two nuclei, the problem of the motion of the nuclei reduces to the motion of a single particle located at $\vec{R}$ with a reduced mass $\mu = M_1 M_2/(M_1 + M_2)$ under the action of a central force in a space-fixed coordinate system with origin at the centre-of-mass.
- Hence the nuclear kinetic energy operator reduces to

$$-\frac{1}{2}\nabla_N^2 = -\frac{1}{2\mu R^2}\left(\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}\right) - \frac{1}{2\mu R^2}\hat{K}^2$$

where $\hat{K}^2$ is the angular momentum operator for the nuclear motion in a space-fixed coordinate system with origin at the centre-of-mass

Comparison of Nuclear and Electronic Motions

- The mass of the nuclei is much larger than that of the electrons, so the time scales of their motions are quite different and we can consider the electronic motion to be occurring for fixed values of R

- So the net wavefunction is written as the sum of the products of nuclear and electronic wavefunctions

$$\Psi(R, \{\vec{r_i}\}) = \sum_a \Phi_a(R; \{\vec{r_i}\}) F_a(\vec{R})$$

- Since, the dependence of the electronic wavefunction on the nuclear coordinates is weaker that the dependence of the nuclear wavefunctions on the nuclear coordinates, we may write

$$\nabla_N^2 \Phi_a(R; \{\vec{r_i}\}) F_a(\vec{R}) \approx \Phi_a(R; \{\vec{r_i}\}) \nabla_N^2 F_a(\vec{R})$$

- This is called the Born–Oppenheimer approximation

- The Schrödinger Equation is written in the form

$$\hat{H} \sum_a \Phi_a F_a = E \sum_a \Phi_a F_a$$

- From this we obtain the equation for the electronic motion

$$\hat{H}_{el}\Phi_a(R; \{\vec{r_i}\}) = E_a(R)\Phi_a(R; \{\vec{r_i}\})$$

since the nuclear operator has no effect on the electronic part

- The terms in $\hat{H}_{el}$ are

$$\hat{H}_{el} = \hat{T}_{el} + \hat{V}$$

$$\hat{T}_{el} = -\sum_i \frac{1}{2}\nabla_i^2$$

$$\hat{V} = -\sum_i \frac{1}{|\vec{r_i} - \vec{R}/2|} - \sum_i \frac{1}{|\vec{r_i} + \vec{R}/2|} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \frac{1}{R}$$

Comparison of Nuclear and Electronic Motions

- R enters the electronic Schrödinger equation as a parameter.
- $E_a(R)$ has to be obtained for each value of R.
- The motion of the nuclei can in turn be considered to occur in a "potential" given by $E_a(R)$.
- The nuclear Schrödinger equation is thus given by

$$\left[-\frac{1}{2\mu R^2} \left(\frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \right) - \frac{1}{2\mu R^2} \hat{K}^2 + E_a(R) \right] F_a(R) = E F_a(R)$$

Electron Terms in a Diatomic Molecule

- The field of several point charges (two in this case) is not centrally symmetric, so the angular momentum of the electrons in a diatomic molecule is not conserved

- A diatomic molecule has a cylindrical symmetry (taken as the $\hat{z}$) axis, and the projection of the angular momentum along this axis, L_z is a conserved quantity

- Thus we can identify electron states by the (quantised) eigenvalues of the $\hat{L}_z$ operator in diatomic molecules

- The electronic eignefunctions Φ_a are simultaneous eigenfunctions of the Hamiltonian and $\hat{L}_z$

- Similar to atoms, we identify the states belonging to different L_z eignevalues by greek letter labels

$\langle L_z \rangle (= \Lambda)$	0	1	2	3
Symbol	Σ	Π	Δ	Φ

Electron Terms in a Diatomic Molecule

- The electronic Hamiltonian is symmeteric w.r.t. reflection in a plane containing the z axis (i.e. the xz or yz planes). This reflection operation changes the sign of the y or the x coordinates, but leaves the sign of z unaltered.
- If under such a reflection, Φ changes to Φ', then Φ and Φ' are different in that the sign of the eigenvalue of $\hat{L}_z$ will be flipped if $\Lambda \neq 0$.
- Since the sign of Λ does not change the energy, states with $\Lambda \neq 0$, that is the Π, Δ, Φ states are doubly degenerate
- The value of Λ for the Σ states is unaffected by the reflection, so Φ' and Φ in such cases can only be different by a multiplying factor: $\Phi' = c\Phi$ (since $\hat{H}_{el}$ is unaltered.
- Since a double reflection is an identity operator, the constant must be ± 1. Hence, there must be two kinds of Σ states, those that flip sign on reflection, and those that do not. These are labelled respectively as Σ^- and Σ^+ states.

Electron Terms in a Diatomic Molecule

- For homonuclear diatomics, another symmetry is possible, namely that of inversion through the centre of mass ($\vec{r} \rightarrow -\vec{r}$)

- Neither $\hat{H}_{el}$ nor $\hat{L}_z$ are altered by this inversion operation, so the only change in the wavefunction Φ under inversion is that of a change in sign

- States for which the wavefunction flips sign under inversion are called ungerade, meaning odd, or u states, while those that do not flip sign under invesion are called gerade meaning even, or g states.

- In addition to this, the state can be identified by it spin multiplicity.

- If S is the sum of the spins of the electrons in the molecules (only open shells matter), then the multiplicity, i.e. the number of spin wavefunctions that are possible for a given spatial wavefunction obeying the Pauli exclusion principle, is $2S + 1$.

Electron Terms in a Diatomic Molecule

- The family of states of a diatomic molecule will thus be designated by the term symbols

Λ	0	1	2	3
Symbol	Σ	Π	Δ	Φ
reflection symmetry	$\Sigma^{\pm}$	Π	Δ	Φ
inversion symmetry	$\Sigma_{g,u}^{\pm}$	$\Pi_{g,u}$	$\Delta_{g,u}$	$\Phi_{g,u}$

- In addition, each term will have a multiplicity label, $2S+1$, so that the full term symbols will be like $^{1}\Sigma_{g}^{+}, ^{2}\Pi_{u}$, etc.
- Most diatomics have a $^{1}\Sigma_{g}^{+}$ ground state, exceptions are O_2 ($^{3}\Sigma_{g}^{+}$) and NO ($^{2}\Pi$).

Electronic Motion in H_2^+

- Let us now consider the electronic motion in H_2^+. The electronic hamiltonian is

$$\hat{H}_{elec} = -\frac{1}{2}\nabla^2 - \frac{1}{|\vec{r} - \vec{r}_A|} - \frac{1}{|\vec{r} - \vec{r}_B|} + \frac{1}{R}$$

- The solutions to the Schrödinger equation are obtained by two methods
    - an approximate method based on linear combinations of atomic orbitals (LCAO)
    - a method based on separation of variables followed by numerical solutions differential equations in one variable
- The LCAO assumes that the electron can "belong" to either or the two atoms, and in the separated atoms limit have atomic hydrogen wavefunction
- Further, when the atoms are combined, the net wavefunction is a linear combination of the atomic wavefunctions centred on either of the two atoms

Electronic Motion in H_2^+

- The net wavefunction (including the spin wavefunction) must possess an exchange anti-symmetry (Pauli's principle), so the spatial part of the wavefunction must have a definite symmetry or antisymmetry
- Thus there are two possible LCAO wavefunctions

$$\Phi_g(R, r) = \frac{1}{\sqrt{2}}[\phi(r_a) + \phi(r_b)]$$

$$\Phi_u(R, r) = \frac{1}{\sqrt{2}}[\phi(r_a) - \phi(r_b)]$$

where $r_a = |\vec{r} - \vec{r}_A|$ and $r_b = |\vec{r} - \vec{r}_B|$, and ϕ is a hydrogenic wavefunction.

- The first form, for the gerade state, is symmetric, the second form, for the ungerade state, is antisymmetric.

- If the ϕ states are 1s hydrogenic states, then the net wavefunction corresponds to a $L = 0$ state.
- Thus the Φ_g and Φ_u wavefunction represent $^2\sigma_g$ and $^2\sigma_u$ states.
- The wavefunctions and probability densities of the two states along the internuclear axis are plotted next.

Electronic Motion in H_2^+
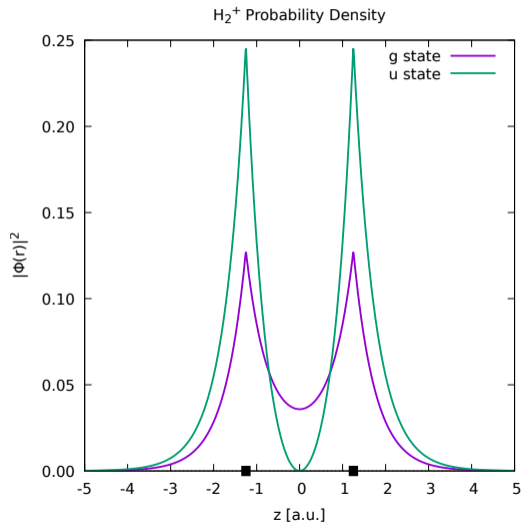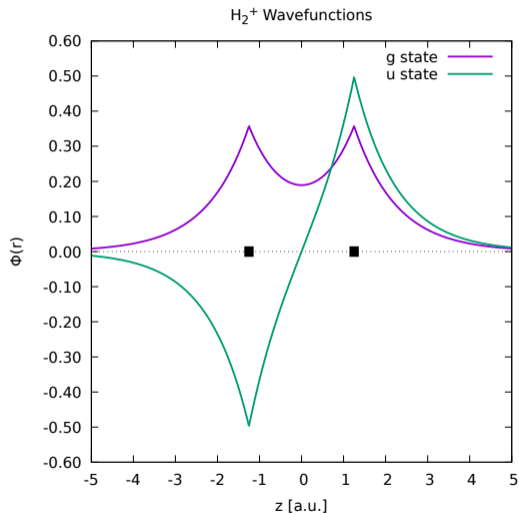
Electronic Motion in H_2^+

- The energy of either of the two states is given by

$$\langle E \rangle = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}$$

- The numerator is given as

$$\int \Phi^* \hat{H} \Phi d\tau = \frac{1}{2} \left[(E_{AA} + E_{BB}) \pm (E_{AB} + E_{BA}) \right]$$

where

$$E_{AA} = \int \phi^*(r_a) \hat{H} \phi(r_a) d\tau \quad \text{and} \quad E_{AB} = \int \phi^*(r_a) \hat{H} \phi(r_b) d\tau$$

We define a overlap integral

$$S(R) = \int \phi(r_a) \phi(r_b) d\tau$$

- Then E_{AA} and E_{AB} can be finally written as

$$E_{AA} = E_0 + \frac{1}{R}(1+R)\exp(-2R)$$

$$E_{AB} = \left[E_0 + \frac{1}{R}\right]S(R) - (1+R)\exp(-R)$$

- The denominator is given as

$$\int \Phi\Phi d\tau = \frac{1}{2}\int \left[\phi(r_a)^*\phi(r_a) + \phi(r_b)^*\phi(r_b) \pm (\phi(r_a)^*\phi(r_b) + \phi(r_b)^*\phi(r_a))\right]d\tau$$
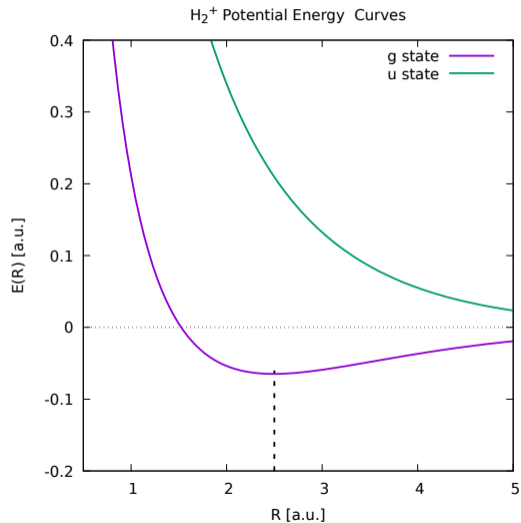$$= 1 + S(R)$$

- Finally, the energies of the two states are

$$E_{g,u} = E_0 + \frac{1}{R} \frac{(1 + R)\exp(-2R) + (1 - 2R^2/3)\exp(-R)}{1 \pm (1 + R + R^2/3)\exp(-R)}$$

- The quantity E_0 is simply the binding energy of the electron to one of the nuclei in the separated atoms limit; if the $\phi(r_a)$ and $\phi(r_b)$ states are 1s states, then $E_0 = 0.5$.
- The two $E_{g,u}(R)$ curves, offset by E_0 is shown next.
- $E_g(R)$ has a minimum near $R = 2.5$ while $E_u(R)$ is always repulsive.

Electronic Motion in H_2^+

Separation of variables

Let us re-consider the electronic hamiltonian of H_2^+ and carry out a separation of variables. The hamiltonian is

$$\hat{H}_{elec} = -\frac{1}{2}\nabla^2 - \frac{1}{|\vec{r} - \vec{r_A}|} - \frac{1}{|\vec{r} - \vec{r_B}|} + \frac{1}{R}$$

If we define the variables

$$\xi = (r_a + r_b)/R, \quad \eta = (r_a - r_b)/R \quad \text{and} \quad \phi$$

where ϕ is the azimuthal angle around the internuclear axis, then the Schrödinger equation can be separated into three single variable equations

$$\Psi(R; \vec{r}) = X(\xi)Y(\eta)Z(\phi)$$

Electronic Motion in H_2^+

The coordinates form the confocal elliptical coordinates, in which loci of constant ξ are ellipses, those of constant η are hyperbolae. The two loci are orthogonal. The two coordinates are dimensionless and the scale of the problem is set by R, the distance between the foci.

The three separated equations are

$$\frac{d}{d\xi}\left[(\xi^2 - 1)\frac{dX}{d\xi}\right] + \left[\frac{R^2}{2}\left(E - \frac{1}{R}\right)\xi^2 + 2R\xi - \frac{m^2}{\xi^2 - 1} + \mu\right]X = 0$$

$$\frac{d}{d\eta}\left[(1 - \eta^2)\frac{dY}{d\eta}\right] + \left[\frac{R^2}{2}\left(E - \frac{1}{R}\right)\xi^2 + \frac{m^2}{1 - \eta 2} + \mu\right]Y = 0$$

$$\left[\frac{d^2}{d\phi^2} + m^2\right]Z = 0$$

These have to be solved numerically

Electronic Motion in H_2

- Let us now consider the electronic motion in H_2. The electronic hamiltonian is

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{r_{AB}}$$

The Schrödinger equation for this can neither be exactly solved, not can separation of variables be effected.

- For later use, we write $\hat{H}$ as

$$\hat{H} = \hat{H}_0(1) + \hat{H}_0(2) + \frac{1}{r_{12}} + \frac{1}{r_{AB}}$$

where

$$\hat{H}_0(i) = -\frac{1}{2}\nabla_i^2 - \frac{1}{r_{iA}} - \frac{1}{r_{iB}}$$

Electronic Motion in H_2

- To solve the He problem, we wrote down a trial wavefunction, based on our knowledge of H wavefunctions
- We take a similar approach to solving the H_2 problem, writing a trial solution based on the wavefunctions of H_2^+. We take the trial wavefunction to be a linear combination of H_2^+ molecular ion wavefunctions
- As before we have to ensure that the exchange symmetry is maintained and Pauli exclusion is obeyed when we write the two electron wavefunction as the product of the spatial and spin parts

The spin wavefunction is either a singlet ($S = 0$) or a triplet ($S = 1$), and the corresponding spin wavefunctions are

$$\chi_{00} = \frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \qquad\qquad S = 0, m = \frac{1}{2}, -\frac{1}{2}$$

$$\chi_{10} = \frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \qquad\qquad S = 1, m = \frac{1}{2}, -\frac{1}{2}$$

$$\chi_{11} = \alpha(1)\alpha(2) \qquad\qquad S = 1, m = \frac{1}{2}, \frac{1}{2}$$

$$\chi_{1-1} = \beta(1)\beta(2) \qquad\qquad S = 1, m = -\frac{1}{2}, -\frac{1}{2}$$

For the spatial part of the wavefunction there are two choices (of H_2^+ molecular orbitals

$$\Phi_g(R, r) = \frac{1}{\sqrt{2}}[\phi(r_a) + \phi(r_b)]$$

$$\Phi_u(R, r) = \frac{1}{\sqrt{2}}[\phi(r_a) - \phi(r_b)]$$

which are respectively, symmetric and antisymmetric w.r.t. exchange.

Electronic Motion in H_2

The net wavefunction can thus be three linear combinations of the spatial wavefunctions for the $S = 0$ case:

$$\Psi_I(1,2) = \Phi_g(1)\Phi_g(2)\chi_{00}$$
$$\Psi_{II}(1,2) = \Phi_u(1)\Phi_u(2)\chi_{00}$$
$$\Psi_{III}(1,2) = \frac{1}{\sqrt{2}}\left[\Phi_g(1)\Phi_u(2) + \Phi_u(1)\Phi_g(2)\right]\chi_{00}$$

and only one spatial wavefunction for the $S = 1$ case

$$\Psi_{IV}(1,2) = \frac{1}{\sqrt{2}}\left[\Phi_g(1)\Phi_u(2) - \Phi_u(1)\Phi_g(2)\right]\chi_{1M} \qquad M = -1, 0, 1$$

The first wavefunction $\Psi_I(1,2)$ represents the lowest state, since Φ_g, and not ϕ_u is the lower energy molecular orbital

The energy corresponding to this is

$$E = \int \Psi_I^*(1,2)\hat{H}\Psi_I(1,2)d\tau_1 d\tau_2$$

$$= 2E_g(R) - \frac{1}{R} + \int |\Phi_g(1)\Phi_g(2)|^2 d\tau_1 d\tau_2$$

The last integral has to be done numerically, and yields $R_0 = 0.8$Å or 1.5 a.u. and $D_e = 2E_0 - E(R_0) = 0.1$ or 2.7 eV.

Electronic Motion in H$_2$

Recalling, that

$$\Phi_g(R, r) = \frac{1}{\sqrt{2}}[\phi(r_a) + \phi(r_b)]$$

$$\Phi_u(R, r) = \frac{1}{\sqrt{2}}[\phi(r_a) - \phi(r_b)]$$

and $\phi(r_a)$ etc. are hydrogen atom 1s wavefunctions, we get

$$\Psi_I(1, 2) = \phi_{1s}(r_{1A})\phi_{1s}(r_{2B}) + \phi_{1s}(r_{2A})\phi_{1s}(r_{B1}) + \phi_{1s}(r_{1A})\phi_{1s}(r_{2A}) + \phi_{1s}(r_{1B})\phi_{1s}(r_{2B})$$

The first two terms represent the case when the two electrons are shared between the two atoms, while the other two terms represent the case when both electrons are associated with one atom.

Thus the $\Psi_I(1,2)$ wavefunction (of the $^1\Sigma_g$ state) is composed of two kinds of contributions: the covalent contribution (first two terms in the expansion in terms of atomic wavefunctions) and the ionic contribution (the second two terms)

$$\Psi_I^{cov}(1,2) = [\phi_{1s}(r_{1A})\phi_{1s}(r_{2B}) + \phi_{1s}(r_{2A})\phi_{1s}(r_{B1})]\chi_{00}$$

Likewise the $\Psi_{IV}(1,2)$ wavefunction (of the $^3\Sigma_u$ state) also has a covalent part (two terms in the expansion in terms of atomic wavefunctions):

$$\Psi_{IV}^{cov}(1,2) = [\phi_{1s}(r_{1A})\phi_{1s}(r_{2B}) - \phi_{1s}(r_{2A})\phi_{1s}(r_{B1})]\chi_{1M}$$

Electronic Motion in H_2

The last two wavefunctions have a special place, as they represent the covalent bonding wavefunctions for the singlet and triplet cases.

These are given the name valence-bond (VB), or Heitler–London wavefunctions, after the persons who proposed those.

The energies corresponding to these wavefunctions are

$$E_{g,u} = 2E_{1s} \pm \frac{J}{1 \pm I^2} \pm \frac{K}{1 \pm I^2} + \frac{1}{R}$$

where

$$I = \int d\tau_1 \phi_{1s}(r_{1A})\phi_{1s}(r_{1B}) = \int d\tau_2 \phi_{1s}(r_{2A})\phi_{1s}(r_{2B})$$

$$J = \int d\tau_1 d\tau_2 |\phi_{1s}(r_{1A})|^2 |\phi_{1s}(r_{2B})|^2 \left(\frac{1}{r_{12}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} \right)$$

$$K = \int d\tau_1 d\tau_2 \phi_{1s}(r_{1A})\phi_{1s}(r_{2B}) \left(\frac{1}{r_{12}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} \right) \phi_{1s}(r_{2A})\phi_{1s}(r_{1B})$$

- A slight improvement in the binding energy and equilibrium bond length can be obtained by mixing Ψ_I and Ψ_{II} (both have the same symmetry) and writing a trial function with an adjustable parameter :
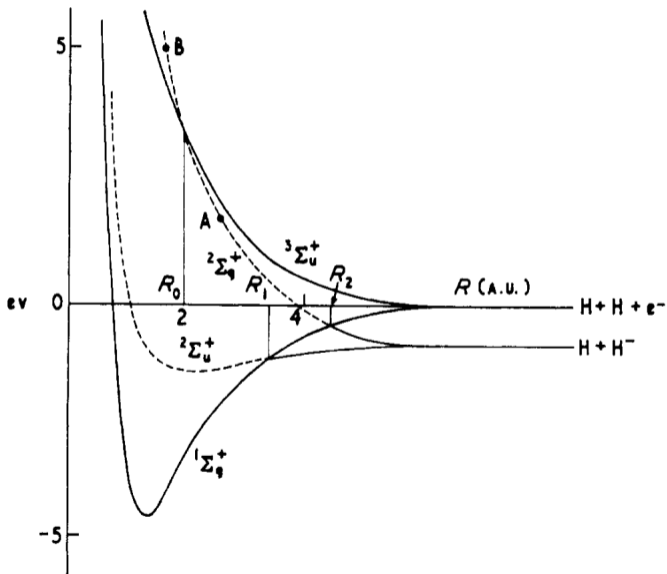
$$\Psi = \Psi_I + \lambda \Psi_{II}$$

and then minimising the energy by the variational principle.

- This yields $R_0 = 0.75$Å or 1.42 a.u. and $D_e = 2E_0 - E(R_0) = 0.147$ or 4.00 eV.

- The same trial wavefunction is the same as that obtained by adjusting the mix of ionic and covalent bonding parts in Φ_I:

$$\Psi = (1 - \lambda)\Psi_I^{cov} + (1 + \lambda)\lambda \Psi_I^{ion}$$

Electronic Motion in H_2