09 - Simple Molecules

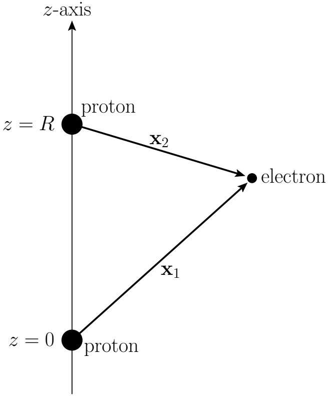
- Aim of Section:
  - Analyze electron and nuclear configurations of simple molecules. Applications are Hydrogen molecule ion and Hydrogen molecule.

Hydrogen Molecule Ion - I

- Hydrogen molecule ion consists of electron orbiting about two protons, and is simplest imaginable molecule.
- Let us investigate whether or not this molecule possesses a bound state: that is, whether or not it possesses a ground-state whose energy is less than that of hydrogen atom (in its ground-state) and free proton.
- According to variation principle, we can deduce that H_2^+ ion has a bound state if we can find any trial state for which total Hamiltonian of system has an expectation value less than that of hydrogen atom and free proton.

Hydrogen Molecule Ion - II

- Suppose that two protons are separated by distance R.
- In fact, let them lie on z-axis, with first at origin, and second at $z = R$.



Hydrogen Molecule Ion - III

- In following, we shall treat protons as essentially stationary.
- This is reasonable, because electron moves far more rapidly than protons.
- Given that electron and protons are subject to similar forces, would expect proton velocities to be approximately factor $\sqrt{m_p/m_e} \simeq 40$ times slower than electron velocity.
- In fact, proton velocities are approximately $(m_p/m_e)^{3/4} \simeq 280$ times slower than electron velocity.
- Neglect of nuclear motion when calculating electronic structure of molecule is known as Born-Oppenheimer approximation.

Hydrogen Molecule Ion - IV

- Let us try

$$|g\rangle = \psi_g(\mathbf{x})\,\chi_\pm = A\,[\psi_{1,0,0}(\mathbf{x}_1) + \psi_{1,0,0}(\mathbf{x}_2)]\,\chi_\pm, \qquad (1)$$

$$|u\rangle = \psi_u(\mathbf{x})\,\chi_\pm = A\,[\psi_{1,0,0}(\mathbf{x}_1) - \psi_{1,0,0}(\mathbf{x}_2)]\,\chi_\pm, \qquad (2)$$

  as our trial electronic states.

- Here,

$$\psi_{1,0,0}(\mathbf{x}) = \frac{1}{\sqrt{\pi}\,a_0^{3/2}}\,\mathrm{e}^{-|\mathbf{x}|/a_0}$$

  is a normalized hydrogen ground-state wavefunction centered on origin.

- Moreover, $\mathbf{x}_{1,2}$ are position vectors of electron with respect to each of protons.

- Finally, $\mathbf{x} = \mathbf{x}_1$ is position vector of electron with respect to origin. Note that $\mathbf{x}_2 = \mathbf{x} - R\,\mathbf{e}_z$.

Hydrogen Molecule Ion - V

- Here, g stands for “gerade” (German for “even”) and u stands for “ungerade” (German for “odd”).
- Obviously, spatial wavefunctions are very simplistic, because they are just linear combination of hydrogen ground-state wavefunctions centered on each proton.
- Note, however, that wavefunctions respect obvious symmetries in problem.

Hydrogen Molecule Ion - VI

- Our first task is to normalize our trial spatial wavefunctions.
- We require that

$$\int |\psi_{g,u}(\mathbf{x})|^2\, d^3\mathbf{x} = 1.$$

- Hence, from (1) and (2), $A = I^{\,-1/2}$, where

$$I = \int \left[|\psi_{1,0,0}(\mathbf{x}_1)|^2 + |\psi_{1,0,0}(\mathbf{x}_2)|^2 \pm 2\,\psi_{1,0,0}(\mathbf{x}_1)\,\psi_{1,0,0}(\mathbf{x}_2)\right] d^3\mathbf{x}.$$

  Here, upper/lower sign corresponds to g/u.
- It follows that

$$I = 2\,(1 \pm J),$$

  with

$$J = \int \psi_{1,0,0}(\mathbf{x}_1)\,\psi_{1,0,0}(\mathbf{x}_2)\,d^3\mathbf{x}.$$

Hydrogen Molecule Ion - VII

- Let us employ standard spherical coordinates, r, θ, ϕ.
- It is easily seen that $|\mathbf{x}_1| = r$ and $|\mathbf{x}_2| = (r^2 + R^2 - 2\,r\,R\,\cos\theta)^{1/2}$.
- Hence,

$$J = 2\int_0^{\infty}\!\!\int_0^{\pi} \exp\left[-x - (x^2 + X^2 - 2\,x\,X\,\cos\theta)^{1/2}\right]\sin\theta\,d\theta\,x^2\,dx,$$

  where $x = r/a_0$ and $X = R/a_0$.
- Here, we have already performed trivial ϕ integral.
- Let $y = (x^2 + X^2 - 2\,x\,X\,\cos\theta)^{1/2}$, so that $d(y^2) = 2\,y\,dy = 2\,x\,X\,\sin\theta\,d\theta$.
- Thus, we get

$$\int_0^{\pi} {\rm e}^{-(x^2+X^2-2\,x\,X\,\cos\theta)^{1/2}}\,\sin\theta\,d\theta = \frac{1}{x\,X}\int_{|x-X|}^{x+X}{\rm e}^{-y}\,y\,dy$$

$$= -\frac{1}{x\,X}\left[{\rm e}^{-(x+X)}\,(1+x+X) - {\rm e}^{-|x-X|}\,(1+|x-X|)\right].$$

Hydrogen Molecule Ion - VIII

- Hence,

$$J = -\frac{2}{X}\,\mathrm{e}^{-X}\int_0^X \left[\mathrm{e}^{-2\,x}\,(1+X+x) - (1+X-x)\right] x\,dx$$
$$-\frac{2}{X}\int_X^\infty \mathrm{e}^{-2\,x}\left[\mathrm{e}^{-X}\,(1+X+x) - \mathrm{e}^{X}\,(1-X+x)\right] x\,dx,$$

which evaluates to

$$J = \mathrm{e}^{-X}\left(1 + X + \frac{X^2}{3}\right). \tag{3}$$

Hydrogen Molecule Ion - IX

- Hamiltonian of electron is written

$$H = -\frac{\hbar^2}{2\,m_e}\,\nabla^2 - \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{1}{|\mathbf{x}_1|}+\frac{1}{|\mathbf{x}_2|}\right).$$

- Note, however, that

$$\left(-\frac{\hbar^2}{2\,m_e}\,\nabla^2 - \frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_{1,2}|}\right)\psi_{1,0,0}(\mathbf{x}_{1,2}) = E_0\,\psi_{1,0,0}(\mathbf{x}_{1,2}),$$

  because $\psi_{1,0,0}(\mathbf{x}_{1,2})$ are hydrogen ground-state wavefunctions.

- It follows that

$$\begin{aligned} H\,\psi_{g,u} &= A\left[-\frac{\hbar^2}{2\,m_e}\,\nabla^2 - \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{1}{|\mathbf{x}_1|}+\frac{1}{|\mathbf{x}_2|}\right)\right][\psi_{1,0,0}(\mathbf{x}_1)\pm\psi_{1,0,0}(\mathbf{x}_2)] \\ &= E_0\,\psi_{g,u} - A\left(\frac{e^2}{4\pi\,\epsilon_0}\right)\left[\frac{\psi_{1,0,0}(\mathbf{x}_1)}{|\mathbf{x}_2|}\pm\frac{\psi_{1,0,0}(\mathbf{x}_2)}{|\mathbf{x}_1|}\right].\end{aligned}$$

Hydrogen Molecule Ion - X

- Hence,

$$\langle H\rangle = E_0 + 4\,A^2\,(D \pm E)\,E_0,$$

  where

$$D = \left\langle \psi_{1,0,0}(\mathbf{x}_1)\left|\frac{a_0}{|\mathbf{x}_2|}\right|\psi_{1,0,0}(\mathbf{x}_1)\right\rangle,$$

$$E = \left\langle \psi_{1,0,0}(\mathbf{x}_1)\left|\frac{a_0}{|\mathbf{x}_1|}\right|\psi_{1,0,0}(\mathbf{x}_2)\right\rangle.$$

Hydrogen Molecule Ion - XI

- Now,

  $$D = 2\int_0^\infty\int_0^\pi \frac{\mathrm{e}^{-2\,x}}{(x^2+X^2-2\,x\,X\,\cos\theta)^{1/2}}\,\sin\theta\,d\theta\,x^2\,dx,$$

  which reduces to

  $$D = \frac{4}{X}\int_0^X \mathrm{e}^{-2\,x}\,x^2\,dx + 4\int_X^\infty \mathrm{e}^{-2\,x}\,x\,dx,$$

  giving

  $$D = \frac{1}{X}\left(1-[1+X]\,\mathrm{e}^{-2\,X}\right). \tag{4}$$

Hydrogen Molecule Ion - XII

- Furthermore,

$$E = 2\int_0^\infty\!\!\int_0^\pi \exp\left[-x-(x^2+X^2-2\,x\,X\,\cos\theta)^{1/2}\right]\sin\theta\,d\theta\,x\,dx,$$

  which reduces to

$$\begin{aligned}E = &-\frac{2}{X}\,\mathrm{e}^{-X}\int_0^X\left[\mathrm{e}^{-2\,x}\,(1+X+x)-(1+X-x)\right]dx\\ &-\frac{2}{X}\int_X^\infty \mathrm{e}^{-2\,x}\left[\mathrm{e}^{-X}\,(1+X+x)-\mathrm{e}^{X}\,(1-X+x)\right]dx,\end{aligned}$$

  yielding

$$E = (1+X)\,\mathrm{e}^{-X}. \tag{5}$$

Hydrogen Molecule Ion - XIII

- Our expression for expectation value of electron Hamiltonian is

  $$\langle H\rangle = \left[1+2\,\frac{(D\pm E)}{(1\pm J)}\right]E_0,$$

  where J, D, and E are specified as functions of $X = R/a_0$ in (3), (4), and (5), respectively.
- In order to obtain total energy of molecule, must add potential energy of two protons to previous expectation value.
- Thus,

  $$E_{\rm total} = \langle H\rangle + \frac{e^2}{4\pi\,\epsilon_0\,R} = \langle H\rangle - \frac{2}{X}\,E_0,$$

  because $E_0 = -e^2/(8\pi\,\epsilon_0\,a_0)$.

Hydrogen Molecule Ion - XIV

- Hence, we can write

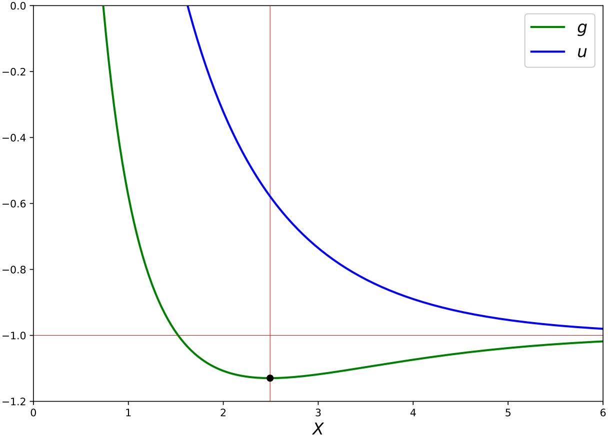
$$E_{\rm total} = -F_{g,u}(R/a_0)\,E_0, \tag{6}$$

where E_0 is hydrogen ground-state energy, and

$$F_{g,u}(X) = -1 + \frac{2}{X}\left[\frac{(1+X)\,{\rm e}^{-2\,X} \pm (1-2\,X^2/3)\,{\rm e}^{-X}}{1 \pm (1+X+X^2/3)\,{\rm e}^{-X}}\right].$$

Hydrogen Molecule Ion - XV

- Functions $F_g(X)$ and $F_u(X)$ are plotted below.



Hydrogen Molecule Ion - XVI

- Recall that in order for H_2^+ ion to possess a bound state, it must have a lower energy than a hydrogen atom (in its ground-state) and a free proton: that is, $E_{\rm total} < E_0$.
- It follows from (6) that a bound state corresponds to $F_{g,u} < -1$.
- Clearly, even trial spatial wavefunction, ψ_g, possesses a bound state, whereas odd trial spatial wavefunction, ψ_u, does not.
- This is not surprising because even wavefunction maximizes electron probability density between two protons, thereby reducing their mutual electrostatic repulsion. On other hand, odd wavefunction does exactly opposite.

Hydrogen Molecule Ion - XVII

- Binding energy of H_2^+ ion is defined as difference between energy of hydrogen atom (in its ground-state) plus a free proton and ground-state energy of ion: that is,

$$E_{\rm bind} = E_0 - E_{\rm total} = (F_g + 1)\, E_0.$$

- According to variational principle, binding energy is greater than or equal to maximum binding energy that can be inferred from previous figure.
- This maximum occurs when $X = 2.49$ and $F_g = -1.13$.
- Thus, our estimates for separation between two protons, and binding energy, for H_2^+ ion are $R = 2.49\, a_0 = 1.32 \times 10^{-10}\,\mathrm{m}$ and $E_{\rm bind} = -0.13\, E_0 = 1.76\,\mathrm{eV}$, respectively.
- Experimentally determined values are $R = 1.06 \times 10^{-10}\,\mathrm{m}$, and $E_{\rm bind} = 2.8\,\mathrm{eV}$, respectively.
- Clearly, our estimates are not particularly accurate.
- However, our calculation does establish, beyond any doubt, existence of bound state of H_2^+ ion.

Hydrogen Molecule Ion - XVIII

- We can improve our calculation by employing trial wavefunction

  $$\psi_{1,0,0}(\mathbf{x}) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \mathrm{e}^{-Z\,|\mathbf{x}|/a_0},$$

  where Z is treated as a variable parameter.
- Repeating previous calculation with new wavefunction, we find that[1]

  $$F_g(X,Z) = -Z^2 + \frac{2\,Z}{X'}\left[\frac{(1+X')\,\mathrm{e}^{-2\,X'} \pm (1-2\,X'^2/3)\,\mathrm{e}^{-X'} + (Z-1)\,X'\,(1+[1+X']\,\mathrm{e}^{-X'})}{1 \pm (1+X'+X'^2/3)\,\mathrm{e}^{-X'})}\right],$$

  where $X' = Z\,X$ and $X = R/a_0$.

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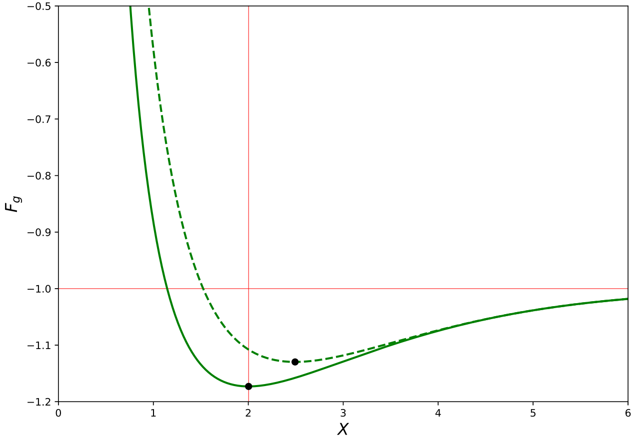
[1] Quantum Mechanics, R. Fitzpatrick, World Scientific 2015

Hydrogen Molecule Ion - XIX

- Function $F_g(X)$ (which has been numerically minimized with respect to Z at each X value) is plotted below (dashed curve is $Z = 1$ case).



Hydrogen Molecule Ion - XX

- Numerically minimizing F_g with respect to X and Z, we find that minimum, $F_g = -1.17$, occurs when $X = 2.00$ and $Z = 1.24$.
- Thus, our improved estimates for separation between two protons, and binding energy, for H_2^+ ion are $R = 2.00\,a_0 = 1.06\times 10^{-10}\,\mathrm{m}$ and $E_\mathrm{bind} = -0.17\,E_0 = 2.35\,\mathrm{eV}$, respectively.
- These estimates are far closer to experimentally determined values than previous estimates.

Proton Motion - I

- Now that we have accounted for fast electron motion in hydrogen molecule ion, let us consider much slower motion of two protons.
- In hydrogen molecule ion ground-state, protons, of mass m_p, move in effective potential

  $$V(R) = F_g(R/a_0)\,|E_0|,$$

  where R is inter-proton distance.

Proton Motion - II

- Let $\mathbf{R}$ be position vector of one proton with respect to other.
- As is well known, two-body dynamical problem equivalent to one-body problem in which particle of reduced mass $m_p/2$, whose position vector with respect to origin is $\mathbf{R}$, moves in central potential $V(|\mathbf{R}|)$.
- Let R, θ, ϕ be spherical coordinates that specify length and orientation of $\mathbf{R}$.

Proton Motion - III

- By analogy with previous analysis of electron moving in central potential in hydrogen atom, can write molecular spatial wavefunction in form

$$\psi(\mathbf{R}) = \Psi(R)\, Y_J^{m_J}(\theta,\phi).$$

- Total orbital angular momentum squared of molecule is $J\,(J+1)\,\hbar$.
- Projection of molecular angular momentum along z-axis is $m_J\,\hbar$.
- Of course, J is non-negative integer, and m_J is integer in range $-J \leq m_J \leq J$.

Proton Motion - IV

- Radial molecular wavefunction satisfies

$$\left[-\frac{\hbar^2}{m_p}\left(\frac{d^2}{dR^2}+\frac{2}{R}\frac{d}{dR}\right)+\frac{J\,(J+1)\,\hbar^2}{m_p\,R^2}+V(R)-E\right]\Psi(R)=0, \tag{7}$$

where E is total (i.e., including electronic) energy of molecule.

Proton Motion - V

- Let $X = R/a_0$, $\hat{E} = E/|E_0|$, and $\Psi(X) = u(X)/X$.
- Because $|E_0| = \hbar^2/(2\,m_e\,a_0^2)$, (7) transforms to give

$$\left[-\epsilon\frac{d^2}{dX^2} + \epsilon\,\frac{J\,(J+1)}{X^2} + F_g(X) - \hat{E}\right] u(X) = 0, \tag{8}$$

where $\epsilon = 2\,m_e/m_p$.

- Expect all terms in previous equation to be $\mathcal{O}(1)$, except ϵ, which is clearly much less than unity.

Proton Motion - VI

- Let us write $X = X_0 + \epsilon^{1/4}\,x$, where $F_g'(X_0) = 0$ and $x \sim \mathcal{O}(1)$.
- What we are effectively saying is that, because $\epsilon \ll 1$, electronic potential, $V(R)$, in which protons move, is strong enough to prevent inter-proton distance from varying too much from its equilibrium value, $R_0 = X_0\,a_0$.
- In fact, variations are order $\varDelta R/R_0 \sim \epsilon^{1/4} \simeq 0.2$ (which is not as small as we would like).
- In this case, can expand electronic potential in Taylor series:

$$F_g(X) = F_g(X_0) + \frac{\epsilon^{1/2}}{2}\,F_g''(X_0)\,x^2 + \frac{\epsilon^{3/4}}{6}\,F_g'''(X_0)\,x^3 + \frac{\epsilon}{24}\,F_g''''(X_0)\,x^4 + \cdots\,.$$

Proton Motion - VII

- (8) becomes

$$\left(-\frac{d^2}{dx^2} + \alpha_2\, x^2 + \mathcal{H}_1 - \mathcal{E}\right) u(x) = 0, \tag{9}$$

where

$$E = \left[F_g(X_0) + \epsilon^{1/2}\,\mathcal{E}\right] |E_0|, \tag{10}$$

$$\mathcal{H}_1 = \epsilon^{1/4}\,\alpha_3\, x^3 + \epsilon^{1/2}\,\alpha_4\, x^4 + \epsilon^{1/2}\,\frac{J\,(J+1)}{X_0^2} + \mathcal{O}(\epsilon^{3/4}), \tag{11}$$

with $\alpha_2 = F_g''(X_0)/2 = 0.141$, $\alpha_3 = F_g'''(X_0)/6 = -0.112$, and $\alpha_4 = F_g''''(X_0)/24 = 0.062$.

Proton Motion - VIII

- Can treat $\mathcal{H}_1$ as perturbation in (9).
- To lowest order, (9) reduces to

$$\left(\frac{d^2}{dx^2} - \alpha_2\, x^2 + \mathcal{E}\right) u(x) = 0.$$

- Let $y = \alpha_2^{1/4}\, x$. Previous equation becomes

$$\left(\frac{d^2}{dy^2} - y^2 + \alpha_2^{-1/2}\, \mathcal{E}\right) u(y) = 0. \tag{12}$$

Proton Motion - IX

- Let $u(y) = \mathrm{e}^{-y^2/2}\,H(y)$.
- (12) transforms to give

$$\frac{d^2H}{dy^2} - 2\,y\,\frac{dH}{dy} + 2\,\lambda\,H = 0. \tag{13}$$

  where $\lambda = (\alpha_2^{-1/2}\,\mathcal{E} - 1)/2$.
- Previous equation is known as Hermite differential equation.
- (13) only possesses square-integrable solutions when $\lambda = n$, where n is non-negative integer.
- Square-integrable solutions are known as (physicist's) Hermite polynomials, and are denoted $H_n(y)$.

Proton Motion - X

- Hermite polynomials have following definition:

$$H_n(y) = (-1)^n\, e^{\,y^2}\, \frac{d^n}{dx^n} \mathrm{e}^{-y^2}.$$

- So,

$$\begin{aligned} H_0(y) &= 1,\\ H_1(y) &= 2\,y,\\ H_2(y) &= 4\,y^2 - 2,\\ H_3(y) &= 8\,y^3 - 12\,y. \end{aligned}$$

- Hermite polynomials are mutually orthogonal:

$$\int_{-\infty}^{\infty} \mathrm{e}^{-y^2}\, H_n(y)\, H_m(y)\, dy = \sqrt{\pi}\, 2^n\, n!\, \delta_{n,m}.$$

Proton Motion - XI

- According to previous analysis, we can write energy of ground-state of hydrogen molecule ion in form

$$E = E_{\rm electron} + E_{\rm vibration}.$$

- Here,

$$E_{\rm electron} = F_g(X_0)\,|E_0| = -15.96\,{\rm eV}$$

  is electronic energy of molecule.

- Moreover,

$$E_{\rm vibration} = \left(\frac{1}{2}+n\right)\hbar\,\omega,$$

  where

$$\hbar\,\omega = 2\,(\epsilon\,\alpha_2)^{1/2}\,|E_0| = 0.34\,{\rm eV},$$

  is energy of molecule due to vibrations in inter-proton distance.

Proton Motion - XII

- Vibrational energy levels are equally spaced with spacing $\hbar\,\omega$.
- Minimum vibrational energy is not zero, but $(1/2)\,\hbar\,\omega$. This is consequence of Heisenberg uncertainty principle: if vibrational displacement were zero then vibrational momentum would be infinite, and vice versa.
- Assuming that electronic and vibrational energy is equally split between kinetic and potential energy (which is actually true), ratio of typical proton to electron velocity can be estimated as

$$\frac{v_p}{v_e} \sim \left(\frac{m_e}{m_p}\,\frac{\hbar\,\omega}{|E_{\rm electron}|}\right)^{1/2} \simeq 3\times 10^{-3}.$$

- Thus, proton motion is indeed much slower than electron motion, which justifies Born-Oppenheimer approximation.

Proton Motion - XIII

- Properly normalized molecular spatial wavefunction takes form

$$\Psi_{n,J,m_J}(\mathbf{R}) = \frac{1}{(a_0\,R_0^{\,2})^{1/2}}\left(\frac{\alpha_2}{\epsilon}\right)^{1/8}\Psi_n(y)\,Y_J^{m_J}(\theta,\phi),$$

where

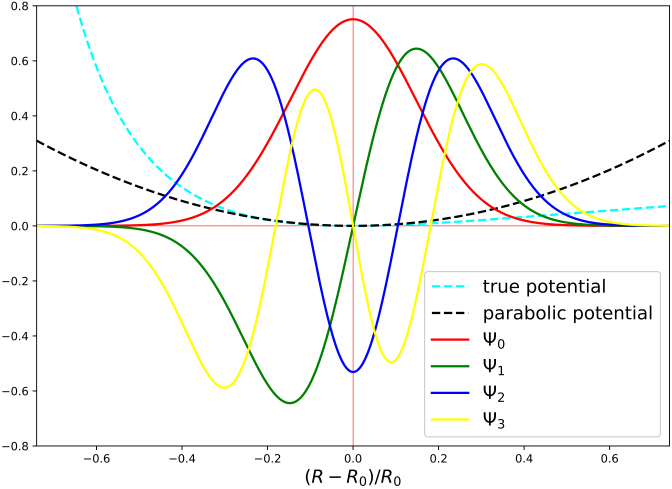
$$y = \left(\frac{\alpha_2}{\epsilon}\right)^{1/4}\left(\frac{R-R_0}{a_0}\right),$$

and

$$\Psi_n(y) = \frac{1}{(\sqrt{\pi}\,2^n\,n!)^{1/2}}\,{\rm e}^{-y^2/2}\,H_n(y).$$

Proton Motion - XIV

- First few radial vibrational wavefunctions are shown below.



Proton Motion - XV

- Treating $\mathcal{H}_1$ in (9) as a perturbation,

$$\mathit{\Delta E} = \epsilon^{1/2}\,|E_0|\left(\langle \mathit{\Psi}_{n,J,m_J}|\mathcal{H}_1|\mathit{\Psi}_{n,J,m_J}\rangle + \sum_{m\neq n}\frac{|\langle \mathit{\Psi}_{n,J,m_J}|\mathcal{H}_1|\mathit{\Psi}_{m,J,m_J}\rangle|^2}{\mathcal{E}_n - \mathcal{E}_m}\right),$$

which reduces to

$$\mathit{\Delta E} = \epsilon^{1/2}\,|E_0|\left\{\int_{-\infty}^{\infty}\mathcal{H}_1(y)\,\mathit{\Psi}_n^{\,2}(y)\,dy + \sum_{k\neq n}\frac{\left[\int_{-\infty}^{\infty}\mathcal{H}_1(y)\,\mathit{\Psi}_n(y)\,\mathit{\Psi}_m(y)\right]^2}{2\,\alpha_2^{-1/2}\,(n-m)}\right\}$$

where

$$\mathcal{H}_1(y) = \epsilon^{1/4}\,\frac{\alpha_3}{\alpha_2^{3/4}}\,y^3 + \epsilon^{1/2}\,\frac{\alpha_4}{\alpha_2}\,y^4 + \epsilon^{1/2}\,\frac{J\,(J+1)}{X_0^2}.$$

Proton Motion - XVI

- It can be demonstrated that

$$\int_{-\infty}^{\infty}\Psi_n^{\,2}(y)\,dy = 1,$$

$$\int_{-\infty}^{\infty}y^3\,\Psi_n^{\,2}(y)\,dy = 0,$$

$$\int_{-\infty}^{\infty}y^4\,\Psi_n^{\,2}(y)\,dy = \frac{3}{4}\,(1+2\,n+2\,n^{\,2}).$$

- Let us define

$$F(n) = \sum_{m\neq n}\frac{\left[\int_{-\infty}^{\infty}y^3\,\Psi_n(y)\,\Psi_m(y)\right]^2}{n-m}.$$

This function can be evaluated numerically. [For instance, $F(0) = -55/40$, $F(1) = -10$, $F(2) = -191/80$.]

Proton Motion - XVII

- Hence, we can write energy of ground-state of hydrogen molecule ion in more accurate form

$$E = E_{\rm electron} + E_{\rm vibration} + E_{\rm rotation}. \tag{14}$$

- Here,

$$E_{\rm vibration} = \left[\frac{1}{2} + n + \beta_3\,F(n) + \beta_4\left(1 + 2\,n + 2\,n^2\right)\right]\hbar\,\omega, \tag{15}$$

  where

$$\beta_3 = \frac{1}{4}\,(\alpha_2\,\epsilon)^{1/2}\,\frac{\alpha_3^2}{\alpha_2^2} = 2.0\times 10^{-3},$$

$$\beta_4 = \frac{3}{8}\,(\epsilon\,\alpha_2)^{1/2}\,\frac{\alpha_4}{\alpha_2^2} = 1.4\times 10^{-2}.$$

- New terms due to anharmonic nature of potential (i.e., fact that it is not purely parabolic), and cause vibrational energy levels to be not quite evenly spaced.

Proton Motion - XVIII

- Moreover,

$$E_{\rm rotation} = J\,(J+1)\,\frac{\hbar^2}{m_p\,R_0^{\,2}}, \tag{16}$$

  is energy that molecule possesses by virtue of its rotation in space.
- Note that

$$\frac{\hbar^2}{m_p\,R_0^{\,2}} = 3.69\times 10^{-3}\,{\rm eV}.$$

- Thus, rotational energy levels just depend on quantum number J.
- Rotational energy levels are much more closely spaced than vibrational energy levels, but are not evenly spaced.

Proton Motion - XIX

- Consider radiative transitions between molecular vibrational-rotational energy levels characterized by quantum numbers n, J, and m_J and n', J', and m_J'.
- We know that probability of such a transition is zero (or very small) unless dipole matrix element

$$\mathbf{d} = \langle \Psi_{n,J,m_J} | e\,\mathbf{x} | \Psi_{n',J',m_J'} \rangle \tag{17}$$

  is non-zero.
- Suppose that $\mathbf{x} = z\,\mathbf{e}_z = r\,\cos\theta\,\mathbf{e}_z$ for sake of definiteness.
- As before, we write $r = R_0 + a_0\,(\epsilon/\alpha_2)^{1/4}\,y$.

Proton Motion - XX

- (17) yields

$$|\mathbf{d}| = e\,a_0\left(\frac{\epsilon}{\alpha_2}\right)^{1/4}\oint Y_J^{m_J}(\theta,\phi)\,\cos\theta\,Y_{J'}^{m_J'}(\theta,\phi)\,d\Omega$$
$$\times\int_{-\infty}^{\infty}\Psi_n(y)\,y\,\Psi_{n'}(y)\,dy.$$

- Angular integral is only non-zero unless $J' = J \pm 1$ and $m_J' = m_J$.
- Had we chose $\mathbf{d} = x\,\mathbf{e}_x$ or $\mathbf{d} = y\,\mathbf{e}_y$ then corresponding angular integrals would only be zero if $J' = J \pm 1$ and $m_J' = m_J \pm 1$.

Proton Motion - XXI

- Follows from integration by parts and $H_n'(y) = 2\,n\,H_{n-1}(y)$ that

$$\int_{-\infty}^{\infty}\Psi_n(y)\,y\,\Psi_{n'}(y)\,dy = \frac{1}{\sqrt{2}}\,(\sqrt{n}\,\delta_{n,n'+1}+\sqrt{n+1}\,\delta_{n,n'-1}).$$

- We deduce that radiative transitions between different vibrational-rotational energy levels are only possible if vibrational and rotational quantum numbers, n and J, both change by unity.

Proton Motion - XXII

- Consider spontaneous radiative transition in which n decreases from $n+1$ to n and J changes from $J+1$ to J.
- According to (14), (15), (16), energy of emitted photon is

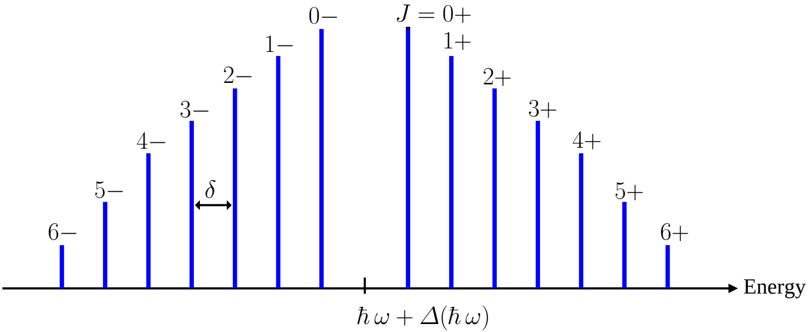
$$E_{n,J+} = \{1+\beta_3\,[F(n+1)-F(n)] + \beta_4\,4\,(n+1)\}\,\hbar\,\omega + 2\,(J+1)\,\frac{\hbar^2}{m_p\,R_0^2}. \tag{18}$$

- Consider spontaneous radiative transition in which n decreases from $n+1$ to n and J changes from J to $J+1$.
- Energy of emitted photon is

$$E_{n,J-} = \{1+\beta_3\,[F(n+1)-F(n)] + \beta_4\,4\,(n+1)\}\,\hbar\,\omega - 2\,(J+1)\,\frac{\hbar^2}{m_p\,R_0^2}. \tag{19}$$

Proton Motion - XXIII

- In first case, change in rotational energy level slightly increases energy of emitted photon. In second case, change in rotational energy level slightly decreases energy of emitted photon.
- Figure below shows schematic molecular vibration-rotation spectrum.



Proton Motion - XXIV

- Spectrum consists of series of equally spaced (in energy/frequency) lines with central line missing.
- For hydrogen molecule ion, we estimate that

$$[\hbar\,\omega + \Delta(\hbar\,\omega)]_{n=1} = 3.51 \times 10^{-1}\,\mathrm{eV},$$
$$[\hbar\,\omega + \Delta(\hbar\,\omega)]_{n=2} = 3.62 \times 10^{-1}\,\mathrm{eV},$$
$$\delta = 7.39 \times 10^{-3}\,\mathrm{eV}.$$

- So shift in center of different series of spectral lines due to anharmonic nature of potential is similar to spacing between successive lines.

Hydrogen Molecule - I

- Hydrogen molecule consists of two electrons orbiting about two protons.
- Let us investigate whether or not this molecule possesses a bound state: that is, whether or not it possesses a ground-state whose energy is less than that of two hydrogen atoms (in their ground-states).
- According to variation principle, we can deduce that H_2 molecule has a bound state if we can find any trial state for which total Hamiltonian of system has an expectation value less than that of two hydrogen atoms.

Hydrogen Molecule - II

- As before, we adopt Born-Oppenheimer approximation in which proton motion is decoupled from electron motion.
- Let two electrons be denoted 1 and 2.
- Let $\mathbf{x}_1$ be position vector of electron 1, and let $\mathbf{x}_2$ be position vector of electron 2.
- Let two protons be situated at origin and at postion vector $\mathbf{R} = R\,\mathbf{e}_z$.

Hydrogen Molecule - III

- Hamiltonian of system written

$$H = H_1 + H_2 + \frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_2 - \mathbf{x}_1|} + \frac{e^2}{4\pi\,\epsilon_0\,R},$$

where

$$H_{1,2} = -\frac{\hbar^2}{2\,m_e}\,\nabla_{1,2}^2 - \frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_{1,2}|} - \frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_{1,2} - \mathbf{R}|}.$$

Hydrogen Molecule - IV

- Let us adopt trial states

  $$|g\rangle = \psi_g(\mathbf{x}_1, \mathbf{x}_2)\, \chi_{\rm singlet},$$

  $$|u\rangle = \psi_u(\mathbf{x}_1, \mathbf{x}_2)\, \chi_{\rm triplet},$$

  where

  $$\psi_{g,u}(\mathbf{x}_1, \mathbf{x}_2) = A\,[\psi_{1,0,0}(\mathbf{x}_1)\, \psi_{1,0,0}(\mathbf{x}_2 - \mathbf{R}) \pm \psi_{1,0,0}(\mathbf{x}_1 - \mathbf{R})\, \psi_{1,0,0}(\mathbf{x}_2)], \tag{20}$$

  and

  $$\psi_{1,0,0}(\mathbf{x}) = \frac{1}{\sqrt{\pi}\, a_0^{3/2}}\, {\rm e}^{-|\mathbf{x}|/a_0}.$$

- As before, upper/lower signs correspond to g/u, but also to overall electron spin zero and unity, respectively.

Hydrogen Molecule - V

- Note that trial wavefunction consists of linear combination of products of atomic (i.e., hydrogen atom) wavefunctions (or orbitals) centered on each proton. This approximation is commonly abbreviated LCAO.
- An alternative approach (which we shall not discuss) would be to use products of molecular (i.e., hydrogen molecule ion) wavefunctions. This approximation of commonly abbreviated MO.

Hydrogen Molecule - VI

- We, first of all, have to normalize trial wavefunction (20).
- Similar analysis to that employed for case of hydrogen molecule ion reveals that

$$A = \frac{1}{\sqrt{2\,(1+J^2)}},$$

where $J(X)$ is defined in (3), and $X = R/a_0$.

Hydrogen Molecule - VII

- Again using similar analysis to hydrogen molecule ion, it is relatively straightforward to show that

$$\langle H_1 + H_2 \rangle = 2 \left[1 + \frac{2\,(D \pm J\,E)}{(1 + J^2)} \right] E_0,$$

  where $D(X)$ and $E(X)$ are defined in (4) and (5).
- It is also easy to show that

$$\left\langle \frac{e^2}{4\pi\,\epsilon_0\,R} \right\rangle = -\frac{2}{X}\,E_0.$$

Hydrogen Molecule - VIII

- Finally, it can be shown that

$$\left\langle \frac{e^2}{4\pi\,\epsilon_0\,|\mathbf{x}_2 - \mathbf{x}_1|} \right\rangle = -\frac{2\,(F \pm G)}{(1 \pm J^2)}\,E_0,$$

where

$$F = \iint \psi^2_{1,0,0}(\mathbf{x}_1)\,\frac{a_0}{|\mathbf{x}_2 - \mathbf{x}_1|}\,\psi^2_{1,0,0}(\mathbf{x}_2 - \mathbf{R})\,d^3\mathbf{x}_1\,d^3\mathbf{x}_2,$$

$$G = \iint \psi_{1,0,0}(\mathbf{x}_1)\,\psi_{1,0,0}(\mathbf{x}_1 - \mathbf{R})\,\frac{a_0}{|\mathbf{x}_2 - \mathbf{x}_1|}\,\psi_{1,0,0}(\mathbf{x}_2)\,\psi_{1,0,0}(\mathbf{x}_2 - \mathbf{R}) \times d^3\mathbf{x}_1\,d^3\mathbf{x}_2.$$

Hydrogen Molecule - IX

- F and G integrals can be evaluated (after much effort)[2] to give

$$F(X) = \frac{1}{X} - \mathrm{e}^{-2X}\left(\frac{1}{X} + \frac{11}{8} + \frac{3}{4}X + \frac{X^2}{6}\right),$$

$$G(X) = \mathrm{e}^{-2X}\left(\frac{5}{8} - \frac{23}{20}X - \frac{3}{5}X^2 - \frac{X^3}{15}\right) + \frac{6}{5}\frac{J^2}{X}\left[\gamma + \ln X + 2\frac{I}{J}E_1(2X) - \frac{I^2}{J^2}E_1(4X)\right],$$

where $\gamma = 0.57721$ is Euler's constant,

$$I(X) = \mathrm{e}^{X}\left(1 - X + \frac{X^2}{3}\right),$$

and

$$E_1(x) = \int_x^\infty \frac{\mathrm{e}^{-t}}{t}\,dt$$

is an exponential integral.

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[2] Y. Sugiura, Z. Physik, **45**, 484 (1927).

Hydrogen Molecule - X

- Putting all of previous analysis together, we deduce that

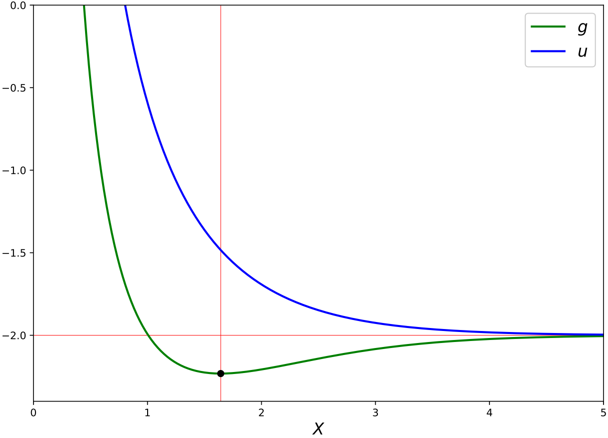
  $$\langle H\rangle = F_{g,u}(R/a_0)\,|E_0|,$$

  where

  $$F_{g,u}(X) = -2\,\left[1+\frac{2\,(D\pm\,J\,E)}{(1\pm J^2)}-\frac{(F\pm G)}{(1\pm J^2)}-\frac{1}{X}\right].$$

Hydrogen Molecule - XI

- Functions $F_g(X)$ and $F_u(X)$ are plotted below.



Hydrogen Molecule - XII

- Recall that in order for H_2 molecule to possess a bound state, it must have a lower energy than two hydrogen atoms (in their ground-states): that is, $\langle H \rangle < 2\,E_0$.
- It follows that a bound state corresponds to $F_{g,u} < -2$.
- Clearly, even trial spatial wavefunction, ψ_g, possesses a bound state, whereas odd trial spatial wavefunction, ψ_u, does not.
- Again, this is not surprising because even wavefunction maximizes electron probability density between two protons, thereby reducing their mutual electrostatic repulsion. On other hand, odd wavefunction does exactly opposite.

Hydrogen Molecule - XIII

- Binding energy of H_2 molecule is defined as difference between energy of two hydrogen atoms (in their ground-state) and ground-state energy of molecule: that is,

$$E_{\rm bind} = 2\,E_0 - \langle H\rangle = (F_g + 2)\,E_0.$$

- According to variational principle, binding energy is greater than or equal to maximum binding energy that can be inferred from previous figure.
- This maximum occurs when $X = 1.64$ and $F_g = -2.23$.
- Thus, our estimates for separation between two protons, and binding energy, for H_2 molecule are $R = 1.64\,a_0$ $= 8.7\times 10^{-11}\,\mathrm{m}$ and $E_{\rm bind} = -0.23\,E_0 = 3.16\,\mathrm{eV}$, respectively.
- Experimentally determined values are $R = 7.4\times 10^{-11}\,\mathrm{m}$, and $E_{\rm bind} = 4.75\,\mathrm{eV}$, respectively.

Hydrogen Molecule - XIV

- Clearly, our estimates are not particularly accurate.
- However, our calculation does establish, beyond any doubt, existence of bound state of H_2 molecule with overall electron spin zero.