

## 7.1 Variational Principle

Suppose that you want to determine the *ground-state* energy  $E_g$  for a system described by  $H$ , but you are unable to solve the time-independent Schrödinger equation.

It is possible to establish an upper bound for  $E_g$  by choosing *any* normalized  $\psi$  (whatsoever) and calculating  $\langle \psi | H | \psi \rangle$ , which *must be*  $\geq E_g$ .

In a sense, this theorem follows from the definition of ‘ground state’, but skeptics can consult the text for a proof.

In practice, this principle allows one to assume a ‘trial wavefunction’ with one or more adjustable parameters, calculate  $\langle \psi | H | \psi \rangle$ , and minimize the resulting value as a function of those parameters, coming arbitrarily close to the actual  $E_g$  (if one has been judicious in one’s choice of trial function). The text provides several examples.

## 7.2 Ground state of helium

The helium atom consists of two electrons in orbit about two protons and two neutrons. Ignoring the fine structure and other small corrections,  $H$  can be written as

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right).$$

Experimentally,  $E_g = -78.975$  eV measured on a scale for which  $E = 0$  corresponds to the two electrons being separately at infinite distance.

There is *no* known solution to the Schrödinger equation corresponding to this  $H$ . The difficulty lies with the last term. If we ignore it, then the Schrödinger equation can be separated into two terms, dependent only on  $\mathbf{r}_1$  and  $\mathbf{r}_2$  individually. The solution to *this* equation is the product of two hydrogenic solutions:  $\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$ , where  $\psi_{100}(\mathbf{r}_1) = \sqrt{\frac{8}{\pi a^3}}e^{-2r_1/a}$ .

It makes sense, then, to use this product wavefunction as the trial function in a variational calculation of  $E_g$ :

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle = -109 \text{ eV} + \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle.$$

After some manipulation but no further approximation, one obtains  $\langle H \rangle = -75 \text{ eV}$ , only slightly larger than the experimental value (-78.975 eV).

Can one expect to do better? Well, yes. One can use a trial function which includes a 'well-chosen' parameter to be varied.

When one of the electrons is somewhat removed from the nucleus, the other electron is free to hover in close to the nucleus. As a consequence, the effective charge of the nucleus, as seen by electron 1, will be reduced somewhat by the 'screening' which results from electron 2, and vice versa.

This effect can be approximated by using a trial function in which the charge of the nucleus,  $Z$ , is allowed to vary so as to minimize  $\langle H \rangle$ .

Accordingly, let  $\psi_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$ .

With some manipulation,

$\langle H \rangle = [-2Z^2 + \frac{27}{4}Z]E_1$ . Setting  $\frac{d}{dZ}\langle H \rangle = 0$  yields  $Z = \frac{27}{16} \doteq 1.69$ , corresponding to a slight screening of the nucleus. The resulting  $E_g = -77.5$  eV, only 2% above the experimental value.

Further improvement in the trial function can reduce the disagreement further.

## 7.3 Hydrogen molecule ion

A second classic application of the variational principle to quantum mechanics is to the singly-ionized hydrogen molecule ion,  $\text{H}_2^+$ :

$$H_{\text{electron}} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right),$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the vectors from each of the two protons to the single electron. If  $\mathbf{R}$  is the vector from proton 1 to proton 2, then  $\mathbf{R} \equiv \mathbf{r}_1 - \mathbf{r}_2$ .

Our main interest is in finding out whether or not this system bonds at all; *i.e.*, whether or not the energy of the ionized molecule (for any value of  $\mathbf{R}$ ) can be less than the total energy of a neutral hydrogen atom plus a single 'distant' proton.

To that end, let's base the trial wf on that of an isolated H atom in its ground state at the origin,  $\psi_g = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$ , and add a second proton, which has been moved from 'far away' to a position  $\mathbf{R}$  relative to the first proton.

If  $R$  is substantially greater than a Bohr radius,  $a$ , we would expect that the electron wf is not changed very much *near the first proton*. On the other hand, we would like to treat the two protons on an equal footing. This suggests that the trial wf take the form  $\psi = A[\psi_g(r_1) + \psi_g(r_2)]$ .

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Normalization:

$$\begin{aligned} 1 &= \int d^3\mathbf{r} |\psi|^2 \\ &= |A|^2 \left[ \int d^3\mathbf{r} |\psi_g(r_1)|^2 + \int d^3\mathbf{r} |\psi_g(r_2)|^2 \right. \\ &\quad \left. + 2\text{Re} \int d^3\mathbf{r} \psi_g^*(r_1) \psi_g(r_2) \right] \\ &= |A|^2 [1 + 1 + 2\text{Re}I]. \end{aligned}$$

$I$ , the overlap integral, is one of a set of integrals found fairly commonly. With some manipulations (see text), it can be shown that  $I = e^{-R/a} \left[ 1 + \frac{R}{a} + \frac{1}{3} \left( \frac{R}{a} \right)^2 \right]$ , yielding  $A(R)$ .

In order to determine whether the ionized H molecule is stable or not, we need to evaluate  $\langle \psi | H_{\text{electron}} | \psi \rangle$ , add to it the potential energy due to proton-proton repulsion, and compare the total with the isolated proton and neutral atom system.

Recall that

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} \right) \psi_g(r_1) = E_1 \psi_g(r_1), \text{ where } E_1 = -13.6 \text{ eV} \text{ and there is a similar expression involving } r_2.$$

Thus, we can write

$$\begin{aligned} H_{\text{electron}} \psi &= A \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \right] [\psi_g(r_1) + \psi_g(r_2)] \\ &= E_1 \psi - A \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{r_2} \psi_g(r_1) + \frac{1}{r_1} \psi_g(r_2) \right]. \end{aligned}$$

It follows that

$$\begin{aligned} \langle H_{\text{electron}} \rangle &= E_1 - 2|A|^2 \frac{e^2}{4\pi\epsilon_0} [\langle \psi_g(r_1) | \frac{1}{r_2} | \psi_g(r_1) \rangle \\ &\quad + \text{Re} \langle \psi_g(r_1) | \frac{1}{r_1} | \psi_g(r_2) \rangle]. \end{aligned}$$

We have come across two more common integrals, known as the direct integral,  $D$ , and the exchange integral,  $X$ :

$$D \equiv a \langle \psi_g(r_1) | \frac{1}{r_2} | \psi_g(r_1) \rangle \text{ and}$$

$$X \equiv a \text{Re} \langle \psi_g(r_1) | \frac{1}{r_1} | \psi_g(r_2) \rangle.$$

These can be evaluated for this particular case

$$\text{to yield } D = \frac{a}{R} - \left(1 + \frac{a}{R}\right) e^{-2R/a} \text{ and}$$

$$X = \left(1 + \frac{R}{a}\right) e^{-R/a}.$$

Putting these together yields an upper limit for the ground-state energy,

$$\langle H_{\text{electron}} \rangle = \left[1 + 2 \frac{(D+X)}{(1+I)}\right] E_1.$$

Adding the potential energy of the two protons,  $V_{pp} = \frac{e^2}{4\pi\epsilon_0 R}$ , the total energy of the ionized H molecule is given in units of  $-E_1$  by

$$F(x) = -1 + \frac{2}{x} \left[ \frac{(1 - \frac{2}{3}x^2)e^{-x} + (1 + x)e^{-2x}}{1 + (1 + x + \frac{1}{3}x^2)e^{-x}} \right],$$

where  $x \equiv R/a$  and  $F(x) = -1$  corresponds to the isolated proton and atom.

Since the term in square brackets is negative for large  $x$ , there is a large range of  $R$  for which the ionized H molecule is more stable than the isolated proton and neutral atom. The lowest energy occurs when  $R$  is approximately 2.4 Bohr radii, or 1.27 Å.

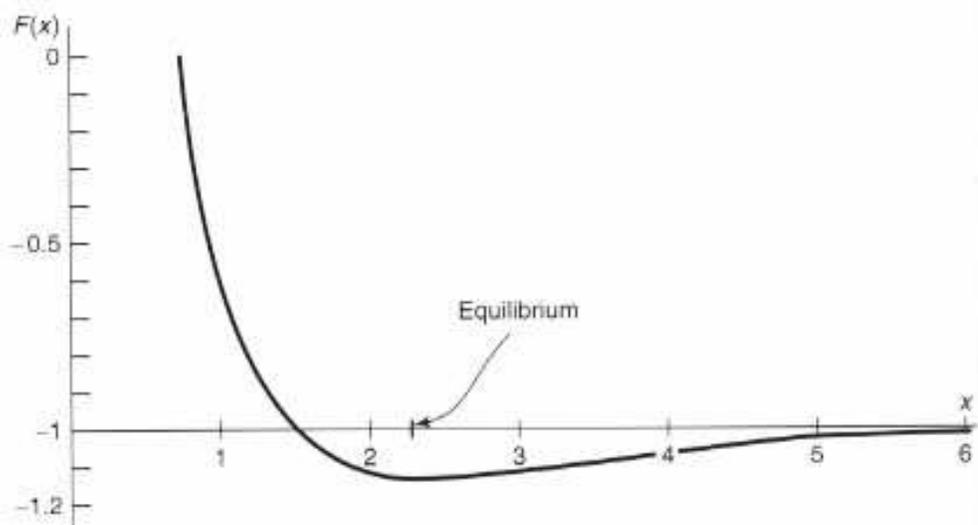


Figure 7.7 - Plot of  $F(x)$  for hydrogen molecule ion, showing bound state.