Quantum Chemistry Course 3033 and 4007 (Part)

The Quantum Chemistry of Atoms and Small Molecules

$$E = \int \psi^* H \quad \psi \, d\tau$$

Junior Sophister Chemistry

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Mathematical tools of the trade

Variable

This is a quantity that has no fixed value (otherwise it would be a *constan*t). Examples: (i) position along a line (measured by x), (ii) time (t), (iii) your varying angle of longitude as you travel on the earth's surface.

Function

This is common from the early years of school algebra. It is an expression involving constants and variables. If it contains only a single variable, say x, such a function could be written $f(x)$. Examples of functions are

$$f(x) = 2x^3 - 4x^2 + 8x - 6$$

$$h(\phi) = \sin 2\phi - 4.8779\tan(\pi/3)$$

In the first $f(x)$ is a cubic function of the variable x. In the second $h(\phi)$ is a function of the angular variable ϕ. The last term in both $f(x)$ and $h(\varphi)$ are constants.

Differential equation

This differs from a simple equation by containing derivatives ($\frac{d}{d\phi}$, $\frac{d^2}{dx^2}$, *etc.*). The *simple* equation $4\cdot 4209x^3 - 7\cdot 5x + 2\cdot 9333 = 0$ has, as solutions, three values of x. Now consider the differential equation

$$\frac{d^2}{dx^2}f(x) - 5\cdot 75\frac{d}{dx}f(x) = 1$$

Solving such an equation entails finding *f(x)*, i.e. *functions of x* (again there might be more than one function), that satisfy the equation.

Operator

You have been using operators all your life. They are things that alter functions when they act on them. Here are some operators, expressed in words:

(1) "Divide what comes next by 2·7 and then add 3".

(2) "Double the following function, take its square root and subtract the original function from the result".

(3) "Differentiate the following function, and then differentiate it again", i.e. "take the second derivative".

An operator has a symbol, so that if P were defined according to (1) as "divide by 2·7 and add 3" and it operates on the $f(x)$ defined above the result is

$$P\,f(x) = \frac{1}{2\cdot 7}f(x) + 3.0 = 0{\cdot}7407x^3 - 1{\cdot}4815x^2 + 2{\cdot}9630x - 0{\cdot}7778$$

Notice that when an operator acts on a function the result is *another function*.

An eigenvalue equation

The last sentence is important. We can express it in symbols as

$$P\ f(x) = g(x)$$

But a special case of the above is conceivable in which the function $g(x)$ produced by the operation is just $f(x)$ multiplied by a constant:

$$P\,f(x) = a\,f(x)$$

This equation is called an *eigenvalue equation*. When most operators P act on functions they change the functions. If P *does* take part in an eigenvalue equation, $f(x)$ is known it is called an *eigenfunctions* and the constant a is called an *eigenvalue.* When you realise that the word *eigen* in German means 'own' or 'property', it is not difficult to see why these words were used. An operator P may have its *own special functions* $f(x)$ such that $\mathsf{P}\,f(x)$ is indeed $f(x)$ multiplied by a constant.

Example: Define the operator P as $\mathsf{P} \equiv \mathrm{d}^2/\mathrm{d}x^2$. Then solve the eigenvalue equation

$$\mathsf{P}\,f(x) = a\,f(x)$$

i.e. find a function of x that, when differentiated twice with respect to x, regenerates the original function multiplied by a constant a. You can think of three:

(1) $f(x) = \sin kx$

(2) $f(x) = \cos kx$

(3) $f(x) = \mathrm{e}^{kx}$

The correct way of verifying these solutions is to substitute the $f(x)$ separately into the left hand side (LHS) and right hand side (RHS) of the equation. Taking solution (2) for example, we have:

LHS: $\mathsf{P}\,f(x) = \mathrm{d}^2/\mathrm{d}x^2 \cos kx = -k^2 \cos kx = -k^2\,f(x)$

RHS: $a\,f(x)$

So the LHS is equal to the RHS on certain conditions. The function $f(x)$ "is a solution of the eigenvalue equation", or equivalently "is an eigenvalue of P" provided $k = \sqrt{}\ a$.

The Schrödinger equation — an eigenvalue equation

The discovery that light particles can be diffracted like light waves prompted Schrödinger to apply a wave equation to them. First let's see how they would be described using the language previously applied to wave motion. We'll suppose that the electrons in the vicinity of an atom or molecule are in a *stationary state*. This equationmeans that they have no time dependence, so they resemble the stationary waves that you see in a violin string or organ pipe or on the surface of your cup of tea after dropping in a lump of sugar. The probability of finding an electron will vary over the atomic region of space and, like the amplitude of the waves in the cases just mentioned, the electron's 'amplitude' would similarly be described by a function. If we confine our discussion to one dimension, such a 'wave function' could be either

$$f(x) = A\sin\frac{2\pi x}{\lambda} \qquad \text{or} \qquad f(x) = A\cos\frac{2\pi x}{\lambda}$$

because either of them describes a wave which repeats after a distance $x = \lambda$. Because it makes the writing easier let's combine these two in the way that we can with sine and cosine functions ($e^{i\theta} = \cos\theta + i\sin\theta$) to get

$$f(x) = A\,e^{2\pi i x/\lambda}$$

Now apply to this function to an equation that describes stationary waves (the '*wave equation*')

$$\frac{d^2 f(x)}{dx^2} = a\,f(x)$$

where a is a constant. The left hand side is

$$\frac{d^2 f(x)}{dx^2} = -A\left(\frac{2\pi}{\lambda}\right)^2 e^{2\pi i x/\lambda}$$

which is in accord with the previous wave (eigenvalue) equation. But the de Broglie equation ($\lambda = h/p$) allows the wavelength λ to be expressed in terms of momentum so that the last equation continues as

$$\frac{d^2 f(x)}{dx^2} = -A\left[\frac{2\pi p}{h}\right]^2 e^{2\pi i x/\lambda} = -\left[\frac{2\pi p}{h}\right]^2 f(x) = -\left[\frac{p}{\hbar}\right]^2 f(x)$$

The final step is to recognize that if this equation is multiplied by $-\hbar^2/2m$ it produces $p^2/2m$ which is the kinetic energy $\frac{1}{2}mv^2$.

$$-\frac{\hbar}{2m}\frac{d^2 f(x)}{dx^2} = \frac{p^2}{2m} f(x) = E\, f(x)$$

If E were the whole of the energy of the particle (as it would be if it were a *free* particle, unaffected by its surroundings) then this eigenvalue equation is

$$\mathscr{H} f(x) = E\, f(x)$$

where $\mathscr{H}$ is the Hamiltonian operator for the system, $\mathscr{H} \equiv -\frac{\hbar}{2m}\frac{d^2}{dx^2}$, 'extracting' the energy E as an eigenvalue. The next step in the development of Schrödinger's equation is to extend $\mathscr{H}$ so as to include not only the kinetic energy but also the potential energy terms $\mathscr{V}$. And finally the space is extended from one dimension to three dimensions so that the Hamiltonian operator now reads

$$\mathscr{H} = -\frac{\hbar}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + \mathscr{V}$$

Denoting the factor in brackets as the Laplacian operator ∇^2, the Schrödinger equation is written

$$\left\{ -\frac{\hbar}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + \mathscr{V}(x, y, z) \right\} \psi(x, y, z) = E\, \psi(x, y, z)$$

or simply

$$\mathscr{H}\, \psi(x, y, z) = E\, \psi(x, y, z)$$

When solved, this equation gives the various *quantum states* of the system through its wave function and energy pairs ψ_1, E_1; ψ_2, E_2; ψ_3, E_3; ψ_4, E_4; . . . The Schrödinger equation is an *eigenvalue equation*, i.e. any function ψ satisfying it must, when operated on by $\mathscr{H}$, regenerate itself on the right hand side, multiplied by a constant E (the energy). Any function doing this is an *eigenfunction* and the energy E is the corresponding *eigenvalue*.

However the only chemical system for which the Schrödinger equation can be solved exactly is the hydrogen atom and such other atoms containing only one electron as He^+, Li^{2+}, Be^{3+} etc. This is because equations describing the motion of a single particle in a *central field* (or spherical potential) such as that of the nucleus are soluble. The states provided by solution of the equation are the familiar ones ψ_{1s}, E_{1s}; ψ_{2s}, E_{2s}; ψ_{2p}, E_{2p}; . . . There is no *general* expression for the eigenfunctions $\{\psi_i\}$, but the functions can be generated. There is, however, a general expression for the energy eigenvalue. It is Bohr's energy equation

$$E_n = -\frac{Z^2 m e^4}{8{\varepsilon_0}^2 h^2} \cdot \frac{1}{n^2}$$

where n is the principal quantum number labelling the electron shells: $n = 1, 2, 3, \ldots$ Z is the number of protons in the nucleus (i.e. the atomic number, which is 1 for hydrogen, but the equation holds for any atom with one electron, such as He^+, Li^{2+}, etc.) As the energy depends only on n (not ℓ), the subshells of the n^{th} shell (ns, np, nd, . . .) all have the same energy. Of course this is not true for atoms containing more than one electron because then an electron in an ns subshell screens the nuclear charge seen by an electron in a np subshell.

The other information provided by the solution to the Schrödinger equation is the set of wave functions or **eigenfunctions** $\{\psi_n\}$which, together with the set of energies or **energy eigenvalues** $\{E_n\}$ are defined by the quantum number n which defines the energy states of the H atom. The lowest energy state is $n = 1$ characterized by the energy E_1 and wave function ψ_1. The next state has energy E_2 and wave function ψ_2 and so on. The H atom has an infinite number of states. Let's look at the first few.

<u>n = 1</u> $\psi_1(1s) = N_1 e^{-r/a}$ $E_1 = -\frac{me^4}{8\varepsilon_0^2 h^2}$

n = 2 $\quad \psi_2(2s) = N_2\left(2 - \frac{r}{a}\right)e^{-r/2a} \qquad E_2 = -\frac{me^4}{8\varepsilon_0^2 h^2}\cdot\frac{1}{4}$

$$\psi_2(2p_x) = N_3 x e^{-r/2a} \qquad E_2 = -\frac{me^4}{8\varepsilon_0^2 h^2}\cdot\frac{1}{4}$$

$$\psi_2(2p_y) = N_3 x e^{-r/2a} \qquad E_2 = -\frac{me^4}{8\varepsilon_0^2 h^2}\cdot\frac{1}{4}$$

$$\psi_2(2p_z) = N_3 x e^{-r/2a} \qquad E_2 = -\frac{me^4}{8\varepsilon_0^2 h^2}\cdot\frac{1}{4}$$

In the H atom (only) the 4 states characterized by $n = 2$ are *energy degenerate* i.e. they have different wave functions, but the same energies. So for the H atom

E_{1s} (non-degenerate, i.e. single energy level)

$< E_{2s} = E_{2px} = E_{2py} = E_{2pz}$ (4-fold degenerate)

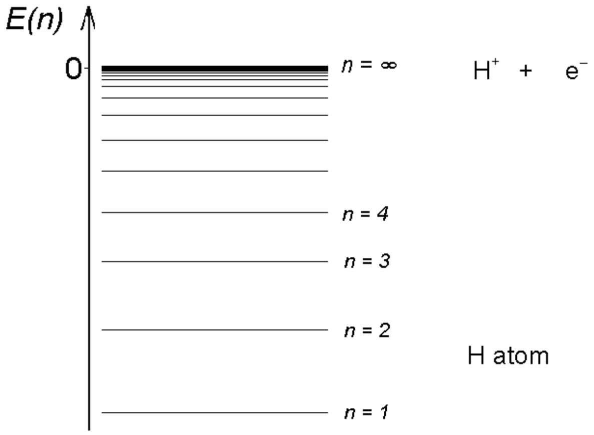
$< E_{3s} = E_{3px} = E_{3py} = E_{3pz} = E_{3\mathrm{dxy}} = E_{3\mathrm{dxz}} = E_{3\mathrm{dyz}} = E_{3\mathrm{dx^2\text{-}y^2}} = E_{3\mathrm{dz^2}}$

(9-fold degenerate)

Representations of the solutions

(a) Energy eigenvalues

This is easy – the general form of the energies E_n shows that they are negative quantities, that they have a distinct minimum value at $n = 1$, the ground state of the H atom. They get progressively closer until they reach their maximum value of $E = 0$ at $n = \infty$, which is the ionization limit. At this point the electron is not associated with the proton and we are dealing with the system $H^+ + e^-$.



The introduction of a second electron such as that in helium removes the spherical symmetry of the Coulomb field as each electron has to negotiate its trajectory through a rather ‘lumpy’ field imposed on the nuclear field by the moving second electron. It is just this *correlated motion* conducted by the electrons that quantum chemists find hard to treat (we’ll discuss *electron correlation* later).

If a second *nucleus* is introduced as in the H_2^+ molecule ion, there is no correlated two-electron motion — the system is a single-electron one, and the Schrödinger equation is soluble[1]. Unlike the case for the hydrogen-like atoms H, He^+, Li^{2+} . . . , the solution does not lead to a general expression to generate the energy levels, but the energies can be evaluated numerically to any desired precision.

As soon as a second electron is introduced, solution of the Schrödinger equation is impossible, and recourse has to be made to approximate methods, in which there is some element.of guesswork in selecting the most suitable approximate wave function. We must first have an understanding of what a wave function is, and its properties.

The nature of the wave function

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[1] This is true only if we neglect that motion of the nuclei which describes the molecular vibration and rotation. This approximation, which works well for most molecules, is the Born-Oppenheimer approximation.

An ‘ideal’ wave function is a solution to the Schrödinger equation, which is a *wave equation*. It therefore describes a wave, whose amplitude varies *in time* if it is a travelling wave and *in space* for a stationary wave. In Chemistry we are mainly (but not exclusively) concerned with electrons etc. in stationary states[2] so that they have ‘amplitudes’ that vary from point to point in space i.e. $\psi \equiv \psi(x, y, z)$ but not in time (Atomic orbitals have shapes which always remain the same.)

But if a wave function has a varying amplitude what is actually varying from point to point in space? An answer proposed by Max Born is that although the wave function doesn’t have a physical meaning, its square – the quantity $|\psi(x, y, z)|^2$ – does, and is the *probability density* of finding the particle around the point x, y, z. It is sometimes given a symbol of its own, ρ, and is obviously also a function of space, i.e. $\rho \equiv \rho(x, y, z)$ Thus according to Born the probability δP of finding a particle in a region of space of volume δV around x, y, z is given by

$$\delta P = \rho(x, y, z)\ \delta V = |\psi(x, y, z)|^2\ \delta V$$

Normalisation

It has been mentioned that when the WF is squared the resulting function $\rho(x,y,z) \equiv |\psi(x,y,z)|^2$ is the particle*’s density function*. This is a ‘number density’, expressing the number of particles per unit volume. When $\rho(x,y,z)$ is multiplied by the volume element $dx\ dy\ dz$ the result $|\psi(x,y,z)|^2\ dx\ dy\ dz$ (number density × volume) gives the probability of finding the particle in volume $dx\ dy\ dz$ around the point x, y, z. The probability of finding it in a *finite* volume $V \equiv V_2 - V_1$ around x, y, z is the integral $\int_{V_1}^{V_2} |\psi|^2\, dV$. Now make V infinite. Then the integral $\int_0^{\infty} |\psi|^2\, dV$ is the *probability of finding the particle somewhere in the whole of space*. And if our WF ψ actually really describes a particle (which is the case in our discussion so far), then this probability is just 1, so thatwe must have

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[2] We don’t always do this – wait for our discussion of tunnelling and the effect of light on molecules.

$$\int_0^\infty |\psi|^2 \, dV = 1$$

This is the *normalisation condition* that must be obeyed by all WFs, as they describe particles that are *somewhere in space*.

How to normalize a wave function

When we first derive or propose a WF ψ' for a system, it may not be normalized. To normalize it, define the *normalized* WF as

$$\psi = N\psi'$$

where N is the normalization constant that is to be calculated. Then

$$1 = N^2 \int_0^\infty |\psi'|^2 \, d\tau$$

So $$N = \sqrt{\frac{1}{\int_0^\infty |\psi'|^2 \, d\tau}}$$

Exercise: Normalize the 1s atomic orbital WF $\psi' = e^{-r/a}$ (a is the Bohr radius — a physical constant)

$$\psi = N\psi' = N\, e^{-r/a}$$

Before using the above relation for N we must convert to a single integration variable, say r. Then since $d\tau = 4\pi r^2 dr$ (the infinitesimal volume of a thin spherical shell of radius r and thickness dr) the required integral is $4\pi \int_0^\infty r^2 e^{-2r/a} dr$. You can do a quick integration of a product and show that since $\int_0^\infty x^2 e^{-bx} dx = 2/b^3$ then $N = \sqrt{\frac{1}{\pi a^3}}$

and so the normalized wave function of the hydrogen atom's 1s atomic orbital is

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

Approximate solutions

If we are prepared to make the effort to eliminate as many sources of numerical inaccuracy as possible then in some cases at least, the use of approximate methods can produce results which, while not exact, are comparable with experiment. In fact, for simple atoms like ground-state helium results calculated by the best methods can be considerably more accurate than those of experiment.

If the Schrödinger equation could be solved we would get the functions ψ_1, ψ_2, ψ_3, . . . for each state, whose energies E_1, E_2, E_3 . . . would emerge at the same time. But since the equation cannot be solved the procedure is to take a trial wave function ψ_i that we think describes the state of interest i, and to tinker with any adjustable parameters which it contains until conditions to be described below are satisfied.

Atomic orbitals and basis functions

There is some degree of skill in making a good guess for ψ_i. You could model the function on the corresponding function of the hydrogen-like atom which is known exactly (for the hydrogen-like atom). It is supposed that the overall shapes of these functions do not change much on addition of other electrons. They define a set of functions known as **atomic orbitals**. These functions provide a *basis for a quantitative description of the electronic states of all atoms.* Some of them are shown in the Table[2] below.

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[2] In this table and in the remainder of the document the normalization factors of wave functions are either not explicitly included or else are written as just *N*. They are of course important for most

Table: Some wave functions and energies of hydrogen-like atoms

$\psi_{1s} = Ne^{-Zr/a_0}$	$E_{1s} = -\dfrac{Z^2me^4}{8\varepsilon_0{}^2h^2}$
$\psi_{2s} = N(2 - Zr/a_0)e^{-Zr/2a_0}$	$E_{2s} = -\dfrac{Z^2me^4}{8\varepsilon_0{}^2h^2}.\dfrac{1}{4}$
$\psi_{2px} = Nr\sin\theta\cos\varphi\ e^{-Zr/2a_0}$	$E_{2px} = -\dfrac{Z^2me^4}{8\varepsilon_0{}^2h^2}.\dfrac{1}{4}$
$\psi_{2py} = Nr\sin\theta\sin\varphi\ e^{-Zr/2a_0}$	$E_{2py} = -\dfrac{Z^2me^4}{8\varepsilon_0{}^2h^2}.\dfrac{1}{4}$
$\psi_{2pz} = Nr\cos\theta\ e^{-Zr/2a_0}$	$E_{2pz} = -\dfrac{Z^2me^4}{8\varepsilon_0{}^2h^2}.\dfrac{1}{4}$
•	
•	
$\psi_{3dxy} = Nr^2\sin^2\theta\cos\varphi e^{-Zr/3a_0}$	$E_{3dxy} = -\dfrac{Z^2me^4}{8\varepsilon_0{}^2h^2}.\dfrac{1}{9}$
•	

Notice that they are all factorised into three components: two are simple angular functions (sin and cos) of θ and ϕ (which do not appear for *s* orbitals since they have spherical symmetry) and the other a radial function in *r* (the instantaneous distance of the electron from the nucleus). The latter is always $r^{n-1}\ e^{-Zr/a_0}$, where *Z* is the nuclear charge, *n* the principal quantum number of the shell and a_0 is the Bohr radius (a physical constant).

If the atomic orbital wave functions ψ_i for the atoms He, Li, Be, . . . are taken to be just the hydrogen-like functions for He^+, Li^{2+}, Be^{3+}, . . . , the calculated energy state E_i would be highly inaccurate, and the reason should be obvious — the hydrogen-like functions do not recognise the presence of any other electrons, which (among other things) screen the nuclear charge.

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calculations that use wave functions, but I want to keep the text as simple as possible. So when you see *N* in an AO wave function just remember that it's made up of physical and mathematical constants.

Allowance is therefore made for nuclear screening by using an effective charge in the atomic orbital's radial component, which is now written $e^{-\zeta r}$, where the parameter ζ is $Z_{\text{effective}}/a_0$, and is fixed by a method to be described below. Provided the best values of ζ are chosen for the atomic orbitals, the functions listed above give good accounts of electronic structures. But how to calculate ζ?

No soluble eigenvalue equation for the He atom!

If you have an *approximate* wave function like one listed in the previous section, can you use it to get the approximate energy? Consider the (hypothetical) case in which the wave function ψ satisfies the Schrödinger equation exactly

$$\mathscr{H}\psi = E\,\psi$$

getting the energy would be trivial — ψ would be an eigenfunction of $\mathscr{H}$ and the constant E the corresponding eigenvalue. So you would just operate on your ψ with $\mathscr{H}$, and whatever you get multiplying ψ is the energy E, and that's that! But an *approximate* ψ does not satisfy the Schrödinger equation so that when you operate on it with $\mathscr{H}$, the result is *not* ψ multiplied by the energy, and so there is no energy to extract. There must be another way.

Go back for a moment to the case where ψ is an eigenfunction of $\mathscr{H}$. Multiply the previous equation by ψ and integrate it. Using the fact that ψ is normalized, we get another expression for the energy.

$$E = \int_0^\infty \psi^* \,\mathscr{H}\psi\, d\tau$$

Performing an integration may be a long-winded way to get the energy when it comes so easily from $E = \mathscr{H}\psi/\psi$, but the integral form would work even when ψ is approximate and *not* an eigenvalue of $\mathscr{H}$. The integral is a definite one — it goes from 0 to infinity and so it is a pure number, not an algebraic expression. And this quantity is what we want — the energy corresponding to the approximate wave function.

The previous section finished at the point at which we had decided to use, as an approximate atomic orbital wave function, one containing $e^{-\zeta r}$, but didn't know how to fix ζ. Here are two ways in which it can be done:

1. Look it up in a book of tables or calculate it by a recipe (Slater's rules – see later).

2. Evaluate it independently yourself using the **Variation Principle** (next).

The variation principle

Write the Hamiltonian operator of a system as $\mathcal{H}$. Suppose you don't know its ground state eigenfunction, but that you have confidence that a set of trial wave functions [ψ_1, ψ_2, ψ_3, …] that you have hit on are not far from the actual eigenfunction, and you wish to find which one is the closest to the eigenfunction. The variation principle states that if you calculate the approximate energies [$\int \psi_1^* \mathcal{H} \psi_1 \, d\tau$, $\int \psi_2^* \mathcal{H} \psi_2 \, d\tau$, $\int \psi_3^* \mathcal{H} \psi_3 \, d\tau$, …] for the set, the function which is closest to the true eigenfunction is the one which corresponds to the lowest energy. In other words, the principle states that

$$\text{if} \qquad E_a \equiv \int \psi_a^* \mathcal{H} \psi_a \, d\tau \qquad < \qquad E_b \equiv \int \psi_b^* \mathcal{H} \psi_b \, d\tau$$

then ψ_a is closer than ψ_b to the actual eigenfunction (which remains unknown!).

Application of the Variation Principle

Once you have decided on the *form* of the wave function — for example the simple exponential $e^{-\zeta r}$ — the best value of the parameter ζ is the one that makes the energy the lowest possible. An obvious way of doing this is to calculate the quantity

$\int_0^\infty \psi^* \mathscr{H} \psi \, d\tau$ with ζ unassigned so that the resulting *E* is a function of ζ. Then put the first derivative equal to zero.

$E \equiv E\,(\zeta)$ i.e. *E* is a known function of ζ

$dE/d\zeta = 0$ condition for minimum *E*

Example 1: The hydrogen atom

Of course we don't need to 'optimise' a trial wave function to describe the H atom because the exact wave functions are known by solving the Schrödinger equation which in this case can be done exactly. But as a simple illustration of the principle we pretend that we are unaware of this knowledge and guess that the H atom's lowest energy state is described by some simple function of electron-proton distance *r*.

(a) Trial function: Simple exponential $\psi = Ne^{-\zeta r}$

The parameter ζ is unknown, and is to be fixed using the Variation Principle. This form for the function ψ, together with the Hamiltonian operator for the H atom

$$\mathscr{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

shows that the energy expression $E = \int_0^\infty \psi^* \mathscr{H} \psi \, d\tau$ is a function of ζ and will be written as $E(\zeta)$.

$$E(\zeta) = N^2 \int_0^\infty e^{-\zeta r} \; [-\frac{\hbar^2}{2\text{m}}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}] \; e^{-\zeta r} \, \text{d}\tau \, .$$

We do not perform the integration explicitly here but accept that the result is

$$E(\zeta) = \frac{\hbar^2}{2m}\zeta^2 - \frac{e^2\zeta}{4\pi\varepsilon_0} \qquad (1)$$

When $\dfrac{dE(\zeta)}{d\zeta}$ is equated to zero to minimize the energy we get

$$\zeta = \frac{e^2 m}{4\pi\varepsilon_0\hbar^2}$$

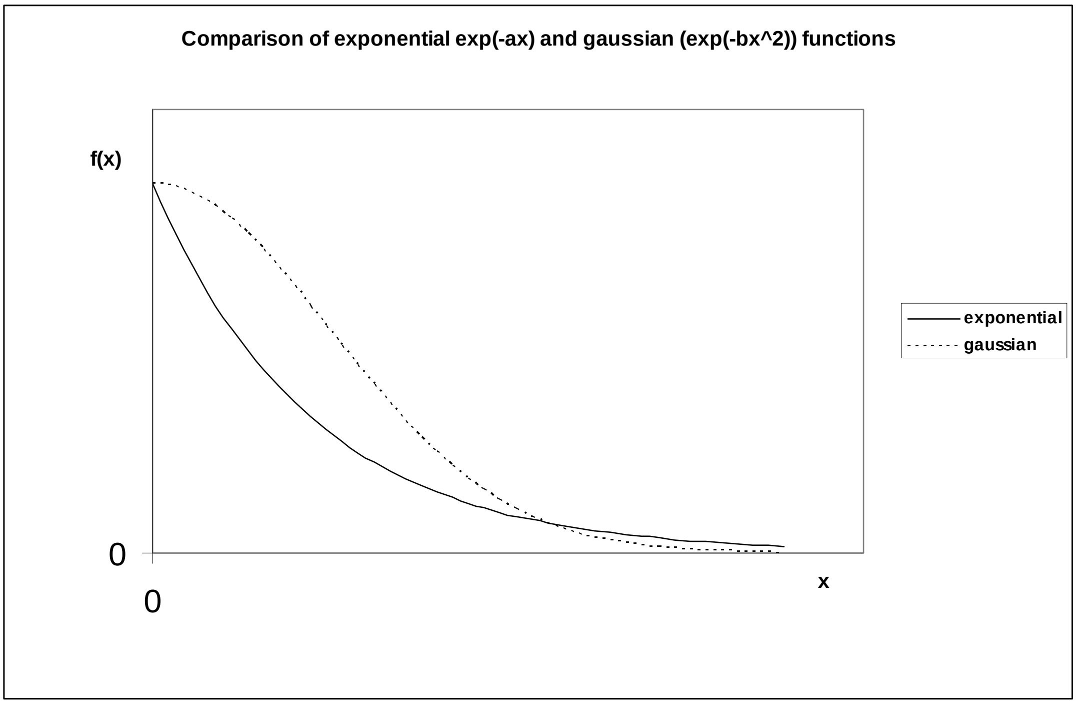
which is just the reciprocal of the Bohr radius $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{e^2 m}$. So we have found that the 'best' function of the simple exponential form is $\psi = Ne^{-r/a_0}$ and that the energy, obtained by substituting the value found for ζ into eq. (1), is

$$E = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2} = -0.5\frac{me^4}{(4\pi\varepsilon_0)^2\hbar^2} \tag{2}$$

But this is the exact energy obtained by Bohr and by exact solution of the Schrödinger equation, which is not surprising because we 'optimised' a function that was already of the correct form.

(b) Trial function: Gaussian $\psi = N\exp(-\zeta r^2)$

The shapes of the exponential exp(–*ax*) and Gaussian exp(–*bx*^{2}) functions are similar insofar as both decay towards zero from definite initial values. But while the Gaussian is flat at $x = 0$, the exponential starts off with a non-zero slope. No amount of adjustment of the parameters *a* or *b* can turn the exponential into a Gaussian or *vice versa*. Since the 1s wave function is known to be $\psi = Ne^{-r/a_0}$ the use of a Gaussian function (whose initial decay is too slow and whose subsequent decay is too rapid) must certainly be wrong, or at best, an approximation. But what would happen if we were to try it[1]?



Comparison of exponential exp(-ax) and gaussian (exp(-bx^2)) functions

The energy function corresponding to eq. (1) for the exponential case (a) is

$$E(\zeta)=\frac{3\hbar^2\zeta}{2m}-\frac{2\sqrt{2}e^2}{4\pi\varepsilon_0\sqrt{\pi}}\sqrt{\zeta} \tag{3}$$

which, when differentiated and set equal to zero to find the energy minimum leads to

$$\frac{3\hbar^2}{2m}-\frac{\sqrt{2}e^2}{4\pi\varepsilon_0\sqrt{\pi}}.\frac{1}{\sqrt{\zeta}}=0$$

giving

$$\zeta=\frac{8}{9\times 4\pi\varepsilon_0\pi a_0^2}$$

and thus the wave function

$$\psi=\exp(-\frac{8}{9\pi a_0^2}r^2)$$

Substituting for ζ into eq. (3) provides the energy,

$$E=-\frac{4}{3\pi}\frac{me^4}{(4\pi\varepsilon_0)^2\hbar^2}\;=\;-0.424\;\frac{me^4}{(4\pi\varepsilon_0)^2\hbar^2} \tag{4}$$

Comparing the energy in (4) with that in (2) shows two important results:

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[1] This is a good example of the principle that one can learn much more from making (controlled) mistakes than by learning supposedly ‘correct’ facts from a textbook or lecturer.

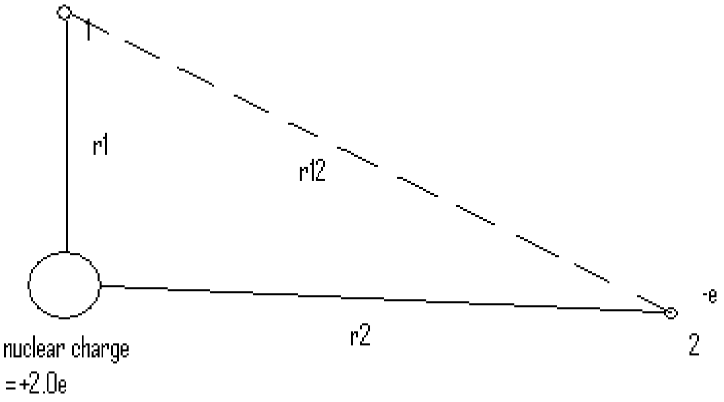
(1) The approximate function provides 85% of the exact energy.

(2) The approximate energy is *greater* than the exact energy.

The first of these may surprise you when you remember that the Gaussian function was not expected to be a good fit to the exponential because of its unsatisfactory behaviour at low *r* and at high *r*. The second is just a vindication of the variation principle.

The helium $1s^2$ configuration

We first write the hamiltonian operator for the helium atom, where some of the labels are illustrated by the diagram. As there are two electrons we call the hamiltonian $\mathscr{H}(1,2)$



$$\mathscr{H}(1,2) = \underset{\text{KE of el. 1}}{-\frac{\hbar^2}{2m}\nabla^2(1)} \underset{\text{el.(1)-nucl. attraction}}{-\frac{2e^2}{4\pi\varepsilon_0 r_1}} \underset{\text{KE of el. 2}}{-\frac{\hbar^2}{2m}\nabla^2(2)} \underset{\text{el(2)-nucl attraction}}{-\frac{2e^2}{4\pi\varepsilon_0 r_2}} + \underset{\text{interelectronic repulsion}}{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}$$

A procedure which simplifies writing is to use atomic units (au), in which several physical constants are declared as *unity*. In au the hamiltonian for helium is

$$H(1,2) = \quad [-½\nabla^2(1) - \frac{2}{r_1}] \quad + \quad [-½\nabla^2(2) - \frac{2}{r_2}] \quad + \quad \frac{1}{r_{12}}$$

$$= \quad H(1) \quad + \quad H(2) \quad + \quad 1/r_{12}$$

Atomic units

e = 1 (electronic charge)

m_e = 1 (electronic mass)

$4\pi\varepsilon_0$ = 1 (appears in the coulomb terms)

$\hbar$ = 1 (appears in the kinetic energy terms)

These imply that the Bohr radius a_0 which is 0.5292×10^{-10} m, is also unity in a.u.:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 1$$

This is the unit of length (bohrs) in atomic units. The ground state energy of the hydrogen atom is

$$E = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2} \qquad = -½ \text{ hartree}$$

where 1 hartree = 4.3595×10^{-18}J = 27.2112 eV, is the a.u. energy unit.

The agreed form of the 1*s* wave function is $\psi_{1s} = \mathrm{N}\, e^{-\zeta r}$, with ζ to be fixed by the variation principle. But this only contains *one* parameter *r* while we have *two* electrons — one at r_1 and the other at r_2. To construct a wave function that describes two electrons in the same orbital $\psi = \mathrm{N}\, e^{-\zeta r}$ we form the product

$$\psi_{1s}(1,2) = \psi_{1s}(1) \times \psi_{1s}(2) = N^2 e^{-\zeta r_1}\, e^{-\zeta r_2}$$

(When $H(1,2)$ operates on $\psi_{1s}(1,2)$, the first factor $\psi_{1s}(1)$ is not affected by $H(2)$, and $\psi_{1s}(2)$ is not affected by $H(1)$. The 3rd term $1/r_{12}$ of course affects both.)

‘Zeroth order’ approximation

In order to get the feel of a quantum chemical calculation let us start slowly by not bothering to use the variation principle to allow for the screening of the nuclear charge, in which case $\psi_{1s}(1) = Ne^{-2r_1}$ and $\psi_{1s}(2) = Ne^{-2r_2}$. We shall also make the drastic (and quite unwarranted) approximation of neglecting the mutual repulsion of the electrons, so that the Hamiltonian is just

$$\begin{aligned} H(1,2) &= \quad [-\tfrac{1}{2}\nabla^2(1) - \frac{2}{r_1}] \quad + \quad [-\tfrac{1}{2}\nabla^2(2) - \frac{2}{r_2}] \\ &= \qquad H(1) \qquad\qquad + \qquad H(2) \end{aligned}$$

Operating on $\psi_{1s}(1,2)$ in accordance with the Schrödinger equation

$$H(1,2)\ \psi_{1s}(1,2) = E\ \psi_{1s}(1,2)$$

We then get

$$\begin{aligned} [H(1) + H(2)]\ \psi_{1s}(1)\ \psi_{1s}(2) &= H(1)\psi_{1s}(1)\ \psi_{1s}(2) + H(2)\psi_{1s}(1)\ \psi_{1s}(2) \\ &= [\,H(1)\psi_{1s}(1)]\ \psi_{1s}(2) + [H(2)\ \psi_{1s}(2)]\ \psi_{1s}(1) \end{aligned}$$

where we have exploited the fact that $H(1)$ operates *only* on $\psi_{1s}(1)$ and $H(2)$ operates *only* on $\psi_{1s}(2)$. But since $H(1)$ and $H(2)$ are hydrogen-like hamiltonians and $\psi_{1s}(1)$ and $\psi_{1s}(2)$ are their eigenfunctions with energy E_{1s} the equation becomes

$$\begin{aligned} H(1,2)\ \psi_{1s}(1,2) &= E_{1s}\psi_{1s}(1,2) + E_{1s}\psi_{1s}(1,2) \\ &= 2E_{1s}\psi_{1s}(1,2) \end{aligned}$$

Since the last equation is an eigenvalue equation we do not need to calculate $\int_0^\infty \varphi^* H\varphi\, d\tau$: the energy eigenvalue is just $2E_{1s}$. With this poor approximation we find the expected result that the electronic energy of the He atom is just twice that of a He^+ ion, i.e. $E = -\dfrac{2^2 me^4}{8\varepsilon_0{}^2 h^2}$. This would be correct were it not for the repulsion of the two electrons, and the fact that the effective nuclear charge is less than 2 because of screening. The numerical value of the energy just calculated is –108·8 eV, to be compared with the measured value of –79·0 eV. Clearly the result calculated by this method is quite unacceptable.

Include electron repulsion and screening

Now use the complete hamiltonian including the $\frac{1}{r_{12}}$ interelectronic repulsion:

$$\psi_{1s}(1,2) = Ne^{-2r_1}\ Ne^{-2r_2}$$

The hamiltonian is

$$H(1,2) \quad = \quad H(1) \ + H(2) \ + \ \frac{1}{r_{12}}$$

and because it now includes the $\frac{1}{r_{12}}$ term, the above $\psi_{1s}(1,2)$ function is not an eigenfunction of $H(1,2)$ as it was before (try it and see!). The energy is

$$E = \int_0^\infty \psi^* \mathscr{H} \psi\, d\tau$$

which evaluates to -74·8319 eV

Next we allow for screening by writing the electronic wave function as

$$\psi_{1s}(1,2) = Ne^{-\zeta r_1}\ Ne^{-\zeta r_2}$$

where the exponent ζ represents the effective nuclear charge and is to be optimized by the Variation Principle. Using this function, and when the helium hamiltonian is substituted for $\mathscr{H}$ in the energy expression $E(\zeta) = \int_0^\infty \psi^* \mathscr{H} \psi\, d\tau$ the result is

$$E(\zeta) = \zeta^2 - 4\zeta + {}^5/_8\zeta$$

Putting $\qquad dE/d\zeta = 0$

we get $\qquad 2\zeta - 4 + {}^5/_8 = 0$

$$\zeta = {}^{27}/_{16} = 1{\cdot}6875$$

This ‘orbital exponent’ is the effective nuclear charge, and is significantly different from the helium atom’s actual nuclear charge $Z = 2$. Substituting ζ in the energy expression gives the electronic energy of helium as

$$E(^{27}/_{16}) \quad = -2{\cdot}8476 \text{ hartrees} = -77{\cdot}5 \text{ eV}$$

Although the agreement is still unsatisfactory, the calculated energy is closer to the measured value of –79·0 eV than that of the previous calculation.

Can the calculation be improved?

To answer this question consider what approximations are left in the treatment. The atomic hamiltonian now contains the exact kinetic and potential energy terms for each of the two electrons, and given that any errors arising from the neglect of relativistic effects are small, what remains? The remaining factor in the energy expression $E = \int_0^\infty \psi^* \mathscr{H} \psi \, d\tau$ is the wave function ψ which is still essentially a simple exponential function borrowed from the hydrogen atom’s ground state, slightly modified. While an exponential function may be appropriate for a one-electron atom it should not be expected to describe an electron under the influence of not only a stationary nuclear charge but also a second electron which could be anywhere in space.

Since it is very difficult to design a function that takes account of the motion of other electrons the best that can be done is to make the function as *flexible* as possible under the constraints of the variation principle. We might for example choose a series of terms, each consisting of an exponential function with a different exponent ζ.:

$$\psi = c_1 e^{-\zeta_1 r} + c_2 e^{-\zeta_2 r} + c_3 e^{-\zeta_3 r} + \cdots$$

Such a function would of course contain a large number of unknown parameters, but these could be optimized by the variation principle. In 1959 using a function of 1078 terms (some exponential, others not) Pekeris obtained an energy of –2·903724375 hartrees (-79·0138 eV) and although it is not corrected for relativistic effects it is more accurate than any experimental measurement to date.

Summary: Attempts to calculate the ground state energy of a He atom

Wave function φ	E (eV)	Comment
e^{-2r}	$-108\cdot8^{(*)}$	No $\frac{1}{r_{12}}$ term in Hamiltonian. No nuclear screening.
e^{-2r}	$-74\cdot8319$	Full Hamiltonian. No nuclear screening.
$e^{-\zeta r}$	$-77\cdot4893$	Full Hamiltonian. Screening included
·	(energy gets	The 1s AO-WF is made more 'flexible' by the inclusion
·	progressively	of terms containing parameters which can be
·	more negative	optimized by the Variation Principle.
(1078-term wave function)	$-79\cdot0138$	Probably the best non-relativistic calculation to date.

$$\boxed{E_{\text{expt.}} = -79\cdot01\ \text{eV}}$$

The Self Consistent Field Method

We have seen that the only *chemical* systems for which the Schrödinger Equation can be solved precisely are *one-electron atoms* (H, He^+, Li^{++}, Be^{+++}, . . . , also called 'hydrogen-like atoms' These atoms are a special case of a more general physical system described as a central field, in which the only field present is spherically symmetric, centered at the origin. For our atoms this would be at the nucleus where all the positive charge is concentrated. A solution of the Schrödinger Equation provides the exact wave functions and energy levels for these atoms.

In the 1928 Hartree got the idea that the central field model could provide an approximate description of many-electron atoms by considering each electron in turn to be moving in the Coulomb field of the nucleus plus a field from the other electrons which was smeared out around the nucleus in such a way as to be spherically symmetrical. The model would then be a central field one, and its Schrödinger Equation could be solved exactly.

The self-consistent field method for atoms (Hartree 1928)

(1) Select one electron (no. **1**) and assign approximate wave functions φ_2, φ_3, . . φ_n to the remaining $n - 1$ electrons on the basis of whether they are 1*s*, 2*s*, 2*p*, . . . etc. A simple assignment could use Slater orbitals for these $n - 1$ electrons.

(2) Use the $n - 1$ functions plus the nuclear charge to represent the electric field through which electron **1** moves. A knowledge of the field allows the Coulomb electrostatic potential energy to be calculated. Remember that charge density is $|\psi|^2$ which is a function of x, y and z, and it is easy to go from a charge distribution via an electric field to a Coulomb energy $V(x, y, z)$ which is plugged into the Hamiltonian as a potential energy term.

(3) The Schrödinger Equation for electron **1** in a central field is solved exactly. (The model is approximate, but the solution is exact for the model.) The lowest-energy function ψ_1 describes electron 1.

> [N.B. The eigenfunctions obtained in 3. describe the distribution of the selected electron moving in the fields of the nuclei and of the remaining $n - 1$ electrons.]

(4) Select another electron (No. **2**), which moves in the field generated by $n - 1$ electrons, a set which is enriched by one of which is described by ψ_1, the wave function of electron **1** obtained in (3). Solve the Schrödinger Equation again getting ψ_2 describing electron **2**.

(5) Select electron **3** which is moving in a field described by a set of functions enriched by the two accurate ones ψ_1 and ψ_2. Solve its Schrödinger Equation and get ψ_3.

Stages in the SCF calculation in which the Schrödinger Equation is solved for electron

$$\begin{array}{ccccccccc}
1 & & 2 & & 3 & & 4 & & n \\
\begin{bmatrix}\varphi_2\\ \varphi_3\\ \varphi_4\\ \varphi_5\\ \cdot\\ \cdot\\ \varphi_n\end{bmatrix} & \longrightarrow & \begin{bmatrix}\psi_1\\ \varphi_3\\ \varphi_4\\ \varphi_5\\ \cdot\\ \cdot\\ \varphi_n\end{bmatrix} & \longrightarrow & \begin{bmatrix}\psi_1\\ \psi_2\\ \varphi_4\\ \varphi_5\\ \cdot\\ \cdot\\ \varphi_n\end{bmatrix} & \longrightarrow & \begin{bmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \varphi_5\\ \cdot\\ \cdot\\ \varphi_n\end{bmatrix} & \longrightarrow \cdots\cdots & \begin{bmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\\ \cdot\\ \cdot\\ \psi_{n-1}\end{bmatrix}
\end{array}$$

Consider electr. 1 and use a set of approx. WFs φ_2 to φ_n to describe the remaining electrons. Solve the S.E. for electr. 1 getting ψ_1

From the soln. for electr. 1 use ψ_1 with the other WFs to solve the SE for electr. 2 getting ψ_2.

Using ψ_1 and ψ_2 and the remaining (approx.) WFs φ_3, φ_3, . . . solve the SE for electr. 3

At this stage electron *n* is moving in a field described by the good-quality functions $\psi_1, \psi_2, \psi_3, \ldots \psi_{n-1}$ Solve the S.E. to get the final function ψ_n. Then return to the start to solve the S.E. for electr. 1 and repeat the cycle to self consistency.

The box shows an overview of the Self Consistent Field method where the initial approximate functions $\varphi_1, \varphi_2, \varphi_3, \ldots$ successively get replaced by more accurate ones $\psi_1, \psi_2, \psi_3, \ldots$

In the 1930s most (all?) of the atoms of the periodic table were treated by SCF. Sometimes improvements were made, at other times the calculation was streamlined with mathematical tricks. A very important innovation was made by Fock, who used antisymmetric functions so that they obeyed the Pauli principle, changing sign when two electrons were interchanged. The results of the final form of the theory, which gave rise to the ‘Hartree-Fock method’, were very good — an impressive fact when you consider the absence of computers at that time: they were obtained by pencil and paper calculations! The calculations were entirely numerical – no analytic wave functions appeared; results appeared as extensive tables of numbers, which today would be replaced by computerized data banks.

Having said that, and even though the Hartree-Fock method remains the best *general* treatment of atoms, it cannot compete with the special treatments of light atoms like helium as were described above. We should see why this is so by examining the limitations of the model. The Schrödinger Equation is being solved for a *single electron* moving in a nuclear field on which has been superimposed a negative charge-cloud to represent the other electrons. This negatively charged electron cloud screens the nuclear charge as indeed it should, but does so in a *static* rather than a *dynamic* way. In fact of course our electron should move in an electric field that fluctuates in response to the movements of the atom's other electrons. The effect on the electrons is that they avoid each other like the perfect flight paths of flies around a light bulb. (Did you ever witness a mid-air fly collision?) The electrons' built-in evasive faculty, called *electron correlation* is mathematically very difficult to account for properly. However it is essential to make allowance for correlation if results of the highest quality are to be obtained. Estimation of the 'correlation energy' is an important feature of modern quantum chemistry.

Why precision?

The electronic energy of the carbon atom calculated by the best Hartree-Fock calculation is –27·6886 hartrees. The correlation energy is about –0·17 hartrees, i.e. about 0·6%. Why is so much effort, manpower and expense made to achieve such accuracy? Converting into chemical energy units using 1 hartree = 2625 kJ mol^{-1} shows that the total electronic energy of the carbon atom is about 72,700 kJ mol^{-1}. But the chemical energies associated with the carbon atom are those energy changes that occur when the carbon atom undergoes chemical reaction. These would be quantities like ΔH, ΔG, E_{act}, … which are of the order of only 100 to 1000 kJ mol^{-1}, i.e. only 0.1 to 1% of the atom's electronic energy! Since they can only be calculated as *energy differences* between those of the initial and final states of the atoms (molecules) these energies have to be known with great accuracy. The carbon atom's correlation energy of 400 kJ mol^{-1} itself is of the same magnitude as its chemical energies so it must not be overlooked if we want to account for the chemical and physical properties of carbon. I selected the carbon atom (only 6 electrons) for this illustration of electronic energies. Large atoms and molecules have huge electronic energies and so the question of precision becomes more acute[2].

Example:

For the esterification reaction the total zero-point electronic energies of the component molecular species were calculated by Gaussian with a moderate basis set.

	CH_3COOH +	$CH_3OH \rightarrow$	CH_3COOCH_3 +	H_2O	
E	−597,943	−301,952	−700,391	−199,526	kJ mol^{-1}

Internal energy difference

$$\begin{aligned}\Delta E &= E_{\text{ester}} + E_{\text{water}} - E_{\text{acetic acid}} - E_{\text{methanol}} \\ &= -700{,}391 - 199{,}526 - (-597{,}943 + 301{,}952) \\ &= -899{,}917 + 899{,}895 \\ &= -22 \text{ kJ mol}^{-1}\end{aligned}$$

As a result of having to subtract two almost equal large numbers (both nearly 1 million) in order to calculate the reaction parameter (−22) shows the inherent problem with the method[3]. Even to have got the correct (negative) sign for the enthalpy of reaction was probably fortuitous!

The first excited state of helium (He)$1s^1 2s^1$

In this section there will be no pursuit of accurate energies as was done for the ground state. Instead, we shall examine the result of promoting one of helium's

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[2] This is the 'Battleship and Admiral' problem of weighing an admiral. His weight is a *small* difference between two *large* measured quantities W_1 and W_2 which are respectively the weight of the battleship with the admiral on board, and of the battleship with the admiral disembarked. Then although the required weight is indeed equal to $W_1 - W_2$, it would not be a reliable measurement of the admiral's weight.

[3] The measured enthalpy difference for glycine-ethanol esterification is ca. −5 kJ mol^{-1}.

electrons to form the first excited configuration He $1s^1 2s^1$. The two atomic orbital wave functions satisfy the hydrogen-atom Schrödinger equation:

$$H(1)\ \varphi_{1s}(1) = E_{1s}\ \varphi_{1s}(1)$$
$$H(2)\ \varphi_{2s}(2) = E_{2s}\ \varphi_{2s}(2)$$

For convenience the 1s and 2s atomic orbital wave functions will be written [1s] and [2s] followed by the label of the electron with which they are associated i.e. (1) or (2). Then the above equations become

$$H(1)\ [1s](1) = E_{1s}\ [1s](1)$$
and $$H(2)\ [2s](2) = E_{2s}\ [2s](2).$$

Electron configuration:

	Wave function	Energy
——↑——— 2s	ϕ_{2s} or "[*2s*]"	E_{2s}
———↑—— 1s	ϕ_{1s} or "[*1s*]"	E_{1s}

The helium hamiltonian may be written as

$$\mathrm{H}(1,2) = \mathrm{H}(1) + \mathrm{H}(2) + 1/r_{12}\ .$$

If the wave function for the two-electron system $\psi(1,2)$ were written in the way it was done for helium's ground configuration $1s^2$ it would be the product

$$\psi(1,2) = [1s](1) \times [2s](2),$$

in which case the energy $E = \int_0^\infty \psi^* H\ \psi\ d\tau$ becomes, on substitution for ψ and H,

$$E = \iint [1s](1)\ [2s](2)\ H(1,2)\ [1s](1)\ [2s](2)\ d\tau_1\ d\tau_2$$

Remembering that $H(1)$ can operate only on [1s](1) and [2s](1) but not on [1s](2) or [2s](2) [and conversely for $H(2)$],

$$H(2)\ [1s](1)\ [2s](2) = [1s](1)\ H(2)\ [2s](2) = [1s](1)\ E_b\ [2s](2),$$

substitution in the energy expression gives

$$E = \iint [1s](1)[2s](2)\ [H(1) + H(2) + 1/r_{12}]\ [1s](1)\ [2s](2)\ d\tau_1\ d\tau_2$$

$= \int[1s](1)\, H(1)\, [1s](1)\, d\tau_1 + \int[2s](2)\, H(2)\, [2s](2)\, d\tau_2 +$

$\iint[1s](1)\, [2s](2)\, 1/r_{12}\, [1s](1)\, [2s](2)\, d\tau_1\, d\tau_2$

$= E_a \int[1s](1)\, [1s](1)\, d\tau_1 + E_b \int[2s](2)\, [2s](2)\, d\tau_2 + \iint\rho(1)\, 1/r_{12}\, \rho(2)\, d\tau_1\, d\tau_2$

$= E_a + E_b + C_{ab}$

where we have

(i) used normalisation:

$\int[1s](1)\, [1s](1)\, d\tau_1 = \int[2s](2)\, [2s](2)\, d\tau_2 = 1$

(ii) introduced the Coulomb integral C_{ab}:

$$C_{ab} = \iint[1s](1)\, [1s](1)\, \frac{1}{r_{12}}\, [2s](2)\, [2s](2)\, d\tau_1\, d\tau_2 = \iint\rho(1)\, \frac{1}{r_{12}}\, \rho(2)\, d\tau_1\, d\tau_2$$

which expresses the repulsion between the charge clouds described by [1s](1) and [2s](2).

The energy expression we have just derived,

$$E = E_{1s} + E_{2s} + C_{1s2s}$$

says that the energy of the (He)$1s^1 2s^1$ configuration is just the energy of the *1s* electron plus that of the *2s* electron plus their Coulombic repulsion energy. It makes sound physical sense, but unfortunately it is wrong. This is because, in writing the wave function as

$$\psi(1,2) = \varphi_{1s}(1)\, \varphi_{2s}(2)$$

we did not take account of the indistinguishability of electrons. We could alternatively have written

$$\psi(1,2) = \varphi_{1s}(2)\, \varphi_{2s}(1),$$

which would have been just as good (or in this case, just as inadequate). The wave function must reflect the indistinguishable character of electrons. Two functions which do this are

$$\psi_{\pm}(1,2) = \frac{1}{\sqrt{2}}\, [\varphi_{1s}(1)\, \varphi_{2s}(2) \pm \varphi_{1s}(2)\, \varphi_{2s}(1)].$$

On substituting in the energy expression

$E_{\pm} = \iint \psi_{\pm}(1,2)\, H(1,2)\, \psi_{\pm}(1,2)\, d\tau_1\, d\tau_2$, we have

$$E_{\pm} = \tfrac{1}{2}\iint \{[1s](1)\,[2s](2) \pm [2s](1)\,[1s](2)\}\ \{H(1) + H(2) + \tfrac{1}{r_{12}}]\}\{[1s](1)\,[2s](2) \pm$$
$$[2s](1)\,[1s](2)]\}d\tau_1\, d\tau_2$$

Recognising the equivalence of terms in (1) and (2), we get, on expanding,

$$E_{\pm} = \tfrac{1}{2}\{2\int[1s](1)\, H(1)\, [1s](1)\, d\tau_1 + 2\int[2s](2)\, H(2)\, [2s](2)\, d\tau_2 +$$
$$2\iint[1s](1)\,[1s](1)\tfrac{1}{r_{12}}\,[2s](2)\,[2s](2)\, d\tau_1\, d\tau_2 \pm 2\iint[1s](1)\,[2s](1)\tfrac{1}{r_{12}}\,[1s](2)\,[2s](2)\, d\tau_1 d\tau_2\}$$
$$= E_{1s}\int[1s](1)\,[1s](1)\, d\tau_1 + E_{2s}\int[2s](2)\,[2s](2)\, d\tau_2 + \iint\rho_{1s}(1)\,\tfrac{1}{r_{12}}\,\rho_{2s}(2)\, d\tau_1\, d\tau_2$$
$$\pm 2\iint[1s](1)\,[2s](1)\,\tfrac{1}{r_{12}}\,[1s](2)\,[2s](2)\, d\tau_1\, d\tau_2$$
$$= E_{1s} + E_{2s} + C_{1s2s} \pm K_{1s2s}$$

where $C_{1s2s} = \iint\rho_{1s}(1)\,\tfrac{1}{r_{12}}\,\rho_{2s}(2)\, d\tau_1\, d\tau_2 \equiv \iint[1s](1)\,[1s](1)\tfrac{1}{r_{12}}\,[2s](2)\,[2s](2)\, d\tau_1\, d\tau_2$

and $K_{1s2s} = \iint[1s](1)\,[2s](1)\,\tfrac{1}{r_{12}}\,[1s](2)\,[2s](2)\, d\tau_1\, d\tau_2$

For C_{1s2s} we have used the fact that the square of the wave function is the electron density function, i.e. $|\,\psi(x, y, z)\,|^2 = \rho(x, y, z)$. The energy expression now contains an aditional term ($\pm K$), where K is called the "exchange integral". Unlike the other terms, K cannot be identified with energy contributions from classical considerations, and arises from the indistinguishability of the electrons. The other implication of this calculation is that the single electron configuration describing the excited state as (He)$1s^1 2s^1$ gives rise to two states, whose energies differ by 2K.

Wave function	Energy
$\frac{1}{\sqrt{2}}\,[[1s](1)\,[2s](2) + [2s](1)\,[1s](2)]$	$E_{1s} + E_{2s} + C_{1s2s} + K_{1s2s}$
$\frac{1}{\sqrt{2}}\,[[1s](1)\,[2s](2) - [2s](1)\,[1s](2)]$	$E_{1s} + E_{2s} + C_{1s2s} - K_{1s2s}$

This result indicates that the same electronic configuration $1s^1\ 2s^1$ can give rise to two energy states, as is indeed found experimentally. Investigations on these states show that there is a rôle played by *electron spin* in forming these states – a subject that we shall now investigate.

Incorporation of electron spin into the helium wave function

A wave function which includes both space and spin parts may be written as a simple product of the separate components. Such a 2-electron helium spin-orbital would be written

$$\Psi(1,2) = \psi(1,2) \times \sigma(1,2)$$

where the factor ψ (1,2) involves the space or 'orbital' functions — in this case the φ_{1s} and/or φ_{2s} atomic orbitals used above — and $\sigma(1,2)$ is the spin function, which is composed of the functions $\alpha(1)$, $\beta(1)$, etc. which describe the electron in the $m_s = +½$ or $m_s = –½$ spin state. **Any total electronic wave function $\Psi(1,2,3,4,\ldots)$ must obey the Pauli Exclusion Principle, i.e. it must be *antisymmetric* to an interchange of two electrons**, or

$$\begin{aligned}\Psi(1, 2, 3, 4, \ldots) &= -\Psi(2, 1, 3, 4, \ldots)\\ &= -\Psi(1, 3, 2, 4, \ldots)\\ &= -\Psi(4, 2, 3, 1, \ldots)\\ &= +\Psi(4, 3, 2, 1, \ldots)\end{aligned}$$

In the last instance an interchange occurs twice, making the process symmetric.

(a) *Helium ground state* $1s^2$

The orbital or spacial function is

$$\psi(1,2) = \varphi_{1s}(1)\ \varphi_{1s}(2)$$

which is symmetric to the interchange of the electron pair. In order for the total function to be antisymmetric as required, it must be combined with an antisymmetric spin function composed of [1s](1), [2s](1), etc. The only permitted function is therefore

$$\Psi(1,2) = \varphi_{1s}(1)\ \varphi_{1s}(2) \times \tfrac{1}{\sqrt{2}}\ [\alpha(1)\,\beta(2)\ -\ \beta(1)\,\alpha(2)]$$

(b) *Helium excited state* $1s^1\ 2s^1$

Here there are two choices of orbital part,

$$\psi_{\pm}(1,2) = \tfrac{1}{\sqrt{2}}\ [\varphi_{1s}(1)\ \varphi_{2s}(2)\ \pm\ \varphi_{2s}(1)\ \varphi_{1s}(2)]$$

one of which (+) is symmetric while the other (–) is antisymmteric. We ensure that the Pauli Principle is obeyed by selecting the appropriate spin function. The permitted combinations are

$$\Psi_{0,0}(1,2) = \tfrac{1}{\sqrt{2}}\ [\varphi_{1s}(1)\ \varphi_{2s}(2) + \varphi_{2s}(1)\ \varphi_{2s}(2)] \times \tfrac{1}{\sqrt{2}}\ [\alpha(1)\ \beta(2)\ - \beta(1)\ \alpha(2)]$$

$$\Psi_{1,1}(1,2) = \tfrac{1}{\sqrt{2}}\ [\varphi_{1s}(1)\ \varphi_{2s}(2) - \varphi_{2s}(1)\ \varphi_{2s}(2)] \times \alpha(1)\ \alpha(2)$$

$$\Psi_{1,0}(1,2) = \tfrac{1}{\sqrt{2}}\ [\varphi_{1s}(1)\ \varphi_{2s}(2) - \varphi_{2s}(1)\ \varphi_{2s}(2)] \times \tfrac{1}{\sqrt{2}}\ [\alpha(1)\ \beta(2)\ + \beta(1)\ \alpha(2)]$$

$$\Psi_{1,-1}(1,2) = \tfrac{1}{\sqrt{2}}\ [\varphi_{1s}(1)\ \varphi_{2s}(2) - \varphi_{2s}(1)\ \varphi_{2s}(2)] \times \beta(1)\ \beta(2).$$

The spin state subscripts (S, M_S) on Ψ are indicated by the spin function. The last three are the components $M_S = 1, 0$ or -1 of the electronic triplet state $S = 1$, while for the first $\Psi_{0,0}$, the spin state $S = 0$ has only one component, $M_S = 0$.

Elect. confign.	Spin state	Energy
$1s^2$	Ground state singlet	$2E_{1s} + C_{1s,1s}$
$1s^1 2s^1$	1st exc. state singlet	$E_{1s} + E_{2s} + C_{1s,2s} + K_{1s,2s}$
$1s^1 2s^1$	1st exc. state	$E_{1s} + E_{2s} + C_{1s,2s} - K_{1s,2s}$

Notes

1. C and K are positive. Therefore in a given electronic configuration ($1s^1 2s^1$) the triplet state level lies lower than that of the singlet (cf. Hund).

2. Original expression of the Pauli Principle: The spin function for the ground state configuration $1s^2$ is $\frac{1}{\sqrt{2}}[\alpha(1)\ \beta(2)\ - \beta(1)\ \alpha(2)]$. But this spin function corresponds

to S = 0 or the condition in which the spins are paired. This means that if two electrons occupy the same orbital, i.e. if they possess the same set of three orbital quantum numbers (n, l, m_l), then they must have different spin quantum numbers $m_s = +½$ and $m_s = -½$

3. Compare the space-parts of the singlet and triplet functions that describe the ($1s^1 2s^1$) configuration. If electrons 1 and 2 in orbital φ are at the same point in space, then $\varphi(1)$, which means $\varphi(x_1,y_1,z_1)$ becomes identical to $\varphi(2)$, which is $\varphi(x_2,y_2,z_2)$. Putting $\alpha(1) = \alpha(2)$ and $\beta(1) = \beta(2)$ makes the triplet state wave functions $\Psi_{1,1}$, $\Psi_{1,0}$ and $\Psi_{1,-1}$ equal to zero (try it!), but not the singlet function $\Psi_{0,0}$. This electron correlation that is built into the triplet functions (i.e. that allows the electrons to move so as to avoid one another) confers greater stability on the triplet state than on the singlet, and thus explains Note #1.

Summary: The lower electronic states of a He atom

Spin-orbital wave function	Energy
1st excited state (singlet) $1s^1 2s^1$	
$\frac{1}{2}[\varphi_{1s}(1)\,\varphi_{2s}(2) + \varphi_{2s}(1)\,\varphi_{2s}(2)] \times [\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$	$E_{1s} + E_{2s} + C + K$
1st excited state (triplet) $1s^1 2s^1$	
$\frac{1}{\sqrt{2}}[\varphi_{1s}(1)\,\varphi_{2s}(2) - \varphi_{2s}(1)\,\varphi_{2s}(2)] \times \alpha(1)\,\alpha(2)$	
$\frac{1}{2}[\varphi_{1s}(1)\,\varphi_{2s}(2) - \varphi_{2s}(1)\,\varphi_{2s}(2)] \times [\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)]$	$E_{1s} + E_{2s} + C - K$
$\frac{1}{\sqrt{2}}[\varphi_{1s}(1)\,\varphi_{2s}(2) - \varphi_{2s}(1)\,\varphi_{2s}(2)] \times \beta(1)\,\beta(2)$.	
Ground state (singlet) $1s^2$	

$$\varphi_{1s}(1)\,\varphi_{1s}(2)\times\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2)\;-\beta(1)\,\alpha(2)] \qquad\qquad 2E_{2s}\;+\;C_{1s1s}$$

Wave functions for atoms with more than two electrons – the Slater determinant

The ground state electron configuration of the lithium atom in its ground state is Li $1s^2\ 2s^1$. On assigning electrons 1, 2 and 3 with appropriate spin WFs to the φ_{1s} and φ_{2s} AOs we must ensure that the antisymmetry principle is obeyed, i.e.

$$\psi(1, 2, 3) = -\psi(2, 1, 3) = -\psi(3, 2, 1) = -\psi(1, 3, 2) = +\psi(2, 3, 1) = +\psi(3, 1, 2)$$

In the 1930s John Slater showed that this is ensured if $\psi(1, 2, 3)$ is written as a determinant:

$$\psi(1,2,3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(3)\alpha(3) \\ \varphi_{1s}(1)\beta(1) & \varphi_{1s}(2)\beta(2) & \varphi_{1s}(3)\beta(3) \\ \varphi_{2s}(1)\alpha(1) & \varphi_{2s}(2)\alpha(2) & \varphi_{2s}(3)\alpha(3) \end{vmatrix}$$

then the Pauli condition is ensured. To show this, consider the following.

1. Interchanging two electrons means interchanging two columns of the determinant. But a property of determinants ensures that if this is done then the determinant changes sign.

2. If we had not assigned different spin wave functions α and β to the two electrons in the $1s$ AO, then rows 1 and 2 would be the same. But if a determinant has two identical rows then that determinant is zero. So two electrons associated with the same AO must have different spins.

3. Put two electrons, say 1 and 2, at the same point in space.

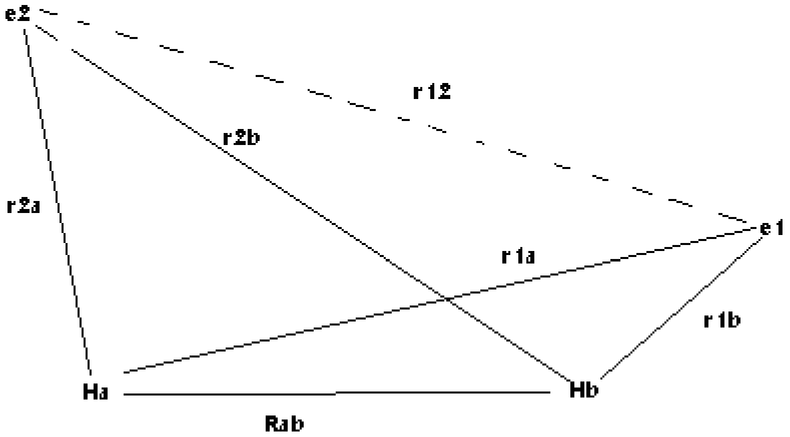
   Then $(x_1, y_1, z_1) = (x_2, y_2, z_2)$,

   i.e. $\varphi_{1s}(1) = \varphi_{1s}(2)$, $\varphi_{2s}(1) = \varphi_{2s}(2)$,

   $\alpha(1) = \alpha(2)$, $\beta(1) = \beta(2)$

   This would make the first two columns the same. But if a determinant has two identical columns then that determinant is zero. So the determinant ensures that the three-electron WF $\psi(1, 2, 3)$ is antisymmetric.

The hydrogen molecule



With the particle separations in the figure the hamiltonian for the molecule is

$$\mathscr{H}(1,2) = \underbrace{[-\tfrac{1}{2}\nabla^2(1) - \frac{1}{r_{1a}} - \frac{1}{r_{1b}}]}_{\text{electron 1}} + \underbrace{[-\tfrac{1}{2}\nabla^2(2) - \frac{1}{r_{2a}} - \frac{1}{r_{2b}}]}_{\text{electron 2}} + \underbrace{\frac{1}{r_{12}}}_{\text{inter-electronic}} + \underbrace{\frac{1}{R_{ab}}}_{\text{inter-nuclear}}$$

The system consists of four particles – two protons and two electrons, all of which contribute to the energy. But we apply the Born-Oppenheimer approximation which recognizes that as the motion of the electrons is much more rapid than that of the nuclei, the energy of the electronic sub-system can be calculated while the nuclei are virtually ‘fixed’ at a separation R_{ab}. This does not prevent us from altering R_{ab}: it just means calculating the electronic energy separately for chosen values of R_{ab}. In other words the Born-Oppenheimer Hamiltonian does not contain terms like $-\frac{\hbar^2}{2M_p}\nabla_a{}^2$ and $-\frac{\hbar^2}{2M_p}\nabla_b{}^2$ for the two protons. However it *does* include internuclear repulsion $\frac{1}{R_{ab}}$ as this will vary over the various internuclear distances that may be selected.

The calculation

We begin by using MO theory in which the basis functions are the well-known bonding and antibonding orbitals, which for electron 1 is

$$\psi_{\pm}(1) = \sqrt{\frac{1}{2(1+S)}}\,[\varphi_a(1) \pm \varphi_b(1)]$$

Here φ_a and φ_b are the 1s atomic orbital functions for the hydrogen atoms *a* and *b*. In line with our sections on the H and He atom calculations we could approximate them as $e^{-\zeta r_a(1)}$ and $e^{-\zeta r_b(1)}$ where $r_a(1)$ and $r_b(1)$ are respectively the distances of electron from the nuclei of atoms *a* and *b*. As before ζ can be fixed by the variation principle. (1) ± $\varphi_b(1)$]. There is a similar function $\psi_{\pm}(2)$ for the second electron. The square-root factor is the normalization constant which involves the overlap integral *S* which here must not be neglected. The basis functions for atoms H_a and H_b could in the simplest case be those of the hydrogen atom $\varphi_a(1) = Ne^{-r_{a1}}$ etc.

The ground state wave function

$$\psi(1,2) = \psi_{+}(1)\ \psi_{+}(2) = \frac{1}{2(1+S)}\,[\varphi_a(1) + \varphi_b(1)] \times [\varphi_a(2) + \varphi_b(2)]$$

is then used to calculate the ground state energy $E = \int_0^\infty \psi^* \mathscr{H} \psi \, d\tau$ using the hamiltonian given at the beginning of this section. When the interatomic distance r_{ab} is varied, the energy minimizes at E = –2.68 eV and R_{ab} = 0.85 Å. The equilibrium bond length of H_2 is 0.74 Å and the measured energy is –4.75 eV. Clearly the result is extremely poor.

Improvements

A very obvious source of error is the use of a nuclear charge of 1.0 when we have already experienced the effects of nuclear screening in the helium atom. Taking the hydrogen 1s functions to be of the form $\varphi = \mathrm{N}\, \mathrm{e}^{-\zeta r}$, with ζ optimised by the variation principle leads to an energy of –3.49 eV and a bond length of 0.732 Å. The interatomic distance is good, the energy is better, but there is still a long way to go. In fact even with the best MO-type wave function the energy improves only to –3.63 eV. Something more fundamental is wrong.

To see what this is, look at the MO wave function $\psi(1,2)$. Multiply it out

$$\psi(1,2) = \frac{1}{2(1+S)}[\varphi_a(1) + \varphi_b(1)] \times [\varphi_a(2) + \varphi_b(2)]$$

$$= \frac{1}{2(1+S)}[\varphi_a(1)\varphi_a(2) + \varphi_b(1)\varphi_b(2) + \varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)]$$

and examine the physical meanings of the resulting terms. The first describes electrons 1 and 2 on the same atom H_a while in the second, the pair are on H_b. These terms are essentially *ionic* structures. In the two remaining terms as the electron pair is shared equally over the atoms, these constitute *covalent* terms. The MO function thus weights ionic and covalent equally, which is not a realistic description of the hydrogen molecule.

Heitler and London (1927), performing the first quantum chemical treatment of a molecule, wrote $\psi(1,2)$ as just the two covalent terms $N[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)]$. Before allowing for screening the energy was –3.14 eV while with screening it came to –3.76 eV, showing that it was a step in the right direction. By allowing for some ionic character by taking a weighted combination of covalent and ionic

$$\psi = \psi_{\mathrm{covalent}} + \lambda\, \psi_{\mathrm{ionic}}$$

where the weighting parameter λ was optimized by the variation principle, the energy came to –4.00 eV.

Admittedly this is still some distance away from the experimentally measured energy of –4.75 eV, but the procedure to get a good result is like that described for helium, i.e. to use very flexible wave functions. Using a 100-term function Kołos and Roothaan in 1960 obtained an energy of –4.7483 eV with an interatomic distance of 0.74 Å. The accuracy of this energy value is already superior to experiment, but (as also for Pekeris' spectacular precision in the calculation of the helium ground state energy in the previous section) the blossoming of computational facilities since 1960 has resulted in only minor improvements to these precisions.

Summary of H_2 calculations

	φ	E (eV)	R_{HH} (Å)	
1. Molecular orbital type				
	e^{-r}	-2·68	0·85	No nuclear screening
	$e^{-\zeta r}$	-3·49	0·732	With screening
	best MO	-3·63		
2. Heitler-London type				
	e^{-r}	-3·14		No nuclear screening
	$e^{-\zeta r}$	-3·76	0·743	With screening
	(covalent) + λ(ionic)	-4·00	0·749	
3. Non-orbital methods				

$\psi(1,2) = \Sigma_i\, c_i\, \lambda_1^m\, \lambda_2^n\, \mu_1^j\, \mu_2^k\, r_{12}^p\, \exp\{-\alpha(\lambda_1 + \lambda_2)\}$ (λ & μ are spheroidal cords of elects 1 & 2)

	-4·72	0·74	(James & Coolidge 1933)
100-term funtion	-4·7483	0·74	(Kołos & Roothaan 1960)

Expt: $E = -4{\cdot}75$ eV $R_{\text{H-H}} = 0{\cdot}74$ Å