

The Schrodinger Equation for Hydrogen and Multi-Electron Systems

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The time-independent Schrodinger equation is always simply,

$$\hat{H}\psi = E\psi \quad (1)$$

where E is the total energy of the system. Here we shall take “the system” to mean just the electrons.

In general, the Hamiltonian operator is the sum of the kinetic energy operator and the potential energy,

$$\hat{H} = \hat{K} + V \quad (2)$$

For a classical particle, the kinetic energy is just $K = \frac{1}{2}mv^2 = \frac{p^2}{2m}$, where $p = mv$ is the momentum. In quantum mechanics, the momentum becomes the momentum operator,

$$p_x \rightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad p_y \rightarrow \hat{p}_y = -i\hbar \frac{\partial}{\partial y} \quad p_z \rightarrow \hat{p}_z = -i\hbar \frac{\partial}{\partial z} \quad (3)$$

And hence,

$$K \rightarrow \hat{K} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad (4)$$

So the one-electron Schrodinger equation is,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi = E\psi \quad (5)$$

where the wavefunction, ψ , is a function of position, \vec{r} . Equations like (5) are called “eigenvalue” equations. Only certain special functions ψ are such that the Hamiltonian operator acts on them so as to produce a result which is just the constant E times the original ψ function. These special functions are called “eigenfunctions” of the Hamiltonian. The corresponding values of E are the eigenvalues. These are the permitted energy levels of the system, the quantum states.

Hydrogen Atom

The potential function is just the electrostatic attraction between the electron and the proton (nucleus), which is $V = -\frac{e^2}{4\pi\epsilon_0 r}$. Note that **negative potential means attractive force**. Hence, the energy levels of a hydrogen atom are given by,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right] \psi = E\psi \quad (6)$$

Without going through the details, the fact that the potential depends only upon the radial coordinate, but not on the angular position, means that the equation, and hence the wavefunction, is “separable”. This means the wavefunction can be expressed as the product of three functions which each depend only upon one of the polar coordinates r, θ, ϕ . Each of these produces a quantum number and the states can be written,

$$\psi = Au_{nl}(r)P_l^m(\cos\theta)e^{im\phi} \quad (7)$$

Here,

n = the principal quantum number = 1,2,3....

l = the orbital angular quantum number, which takes integral values *less than* n , so that $n = 1$ has only $l=0$; $n = 2$ has $l = 0$ or 1, etc.;

m is the azimuthal quantum number, taking values from $-l$ to $+l$.

You do not need to take my word for it that the angular states are described by l and m because this has been covered already in the notes on angular momentum. Solving the hydrogen atom equations just derives it again – for that special case.

So we already know that m can take values from $-l$ to $+l$. What (7) does tell you is the explicit form of the wavefunction as a function of the polar angles θ, ϕ . The functions P_l^m are called the associated Legendre functions. The term A is just a normalisation constant.

[Recall that normalisation requires that $\int \psi^* \psi dx dy dz = 1$, where the integration is carried out over the whole of space. This allows the constant A to be found].

NB: The normalised combinations are called the spherical harmonics

$$Y_l^m(\theta, \phi) = AP_l^m(\cos\theta)e^{im\phi} \quad (8)$$

The radial functions are found in terms of the Laguerre polynomials. They depend upon both the quantum numbers n and l .

The energy levels of hydrogen, in the non-relativistic approximation represented by the Schrodinger equation, and neglecting spin effects, depend only upon the principle quantum number, n . Explicitly they are,

$$E_n = -\frac{\alpha^2 m_e c^2}{2n^2} \quad (9)$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137}$. The ground state energy is thus -13.6eV. Note that the

energies are negative because they represent bound states. As n increases the energy increases, i.e., the magnitude of the negative energy decreases.

The first few hydrogen wavefunctions in explicit normalised form are,

$$n=1, l=0 \quad \psi = \frac{1}{\sqrt{\pi}a_0^{3/2}} \exp\left\{-\frac{r}{a_0}\right\} \quad (\text{Ground State, Energy } E_1) \quad (10)$$

$$n=2, l=0 \quad \psi = \frac{1}{\sqrt{4\pi}(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) \exp\left\{-\frac{r}{2a_0}\right\} \quad (\text{Energy } E_2) \quad (11)$$

$$n=2, l=1, m=0 \quad \psi = \frac{\sqrt{3}}{\sqrt{4\pi}(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) \exp\left\{-\frac{r}{2a_0}\right\} \cos\theta \quad (\text{Energy } E_2) \quad (12)$$

$$n = 2, l = 1, m = \pm 1 \quad \psi = \frac{\mp 1}{\sqrt{8\pi}(2a_0)^{3/2}} \cdot \frac{r}{a_0} \exp\left\{-\frac{r}{2a_0}\right\} \sin \theta \cdot e^{\pm i\phi} \quad (\text{Energy } E_2) \quad (13)$$

where $a_0 = \frac{\hbar}{\alpha m_e c} = 0.53 \times 10^{-10}$ metres is the Bohr radius, the approximate radius of the hydrogen atom.

Multielectron Atoms or Ions (Single Nucleus)

Throughout we ignore the dynamical degrees of freedom associated with the nuclei, and we also ignore spin effects. Considering only the electrons without spin, the Schrodinger equation for N electrons at positions \bar{r}_i from the nucleus, where $i = 1$ to N , is,

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 |\bar{r}_i - \bar{r}_j|} \right] \Psi = E\Psi \quad (14)$$

E is the total energy of all N electrons. The wavefunction depends on all N electrons coordinates, $\Psi(\bar{r}_1, \bar{r}_2, \bar{r}_3, \dots, \bar{r}_N)$.

The first term in (14) is the sum of the kinetic energies of all N electrons, expressed in terms of the del-squared operator which acts on that electron's position coordinate.

The second term is the sum of the attractive (i.e., negative) potential between each electron and the nucleus, which is taken to have atomic number Z (hence its charge is Ze). If this were a neutral atom then $Z = N$, but for a positive ion $Z > N$, or for a negative ion $Z < N$.

The third term is the repulsive (i.e., positive) potential between every possible pair of electrons. The sum covers all pairs, e.g., 12, 13, 14..., plus 23, 24, ..., etc. This involves the distance between the electrons, i.e., $|\bar{r}_i - \bar{r}_j|$. If this term were omitted there would be no interaction between the electrons, and the exact solution to (14) could be written simply as the product of hydrogenic wavefunctions, one factor for each electron. But the presence of this term, the electron-electron Coulomb repulsion, modifies the wavefunctions and their energies.

Equations like (14) cannot be solved exactly in 'closed form' (i.e., algebraically). Instead approximate solutions are required, usual accomplished numerically by computer. Techniques of solution include perturbation theory and variational methods like the Hartree-Fock method.

Multielectron Molecules (Many Nuclei)

The difference from (14) is that we now have M nuclei at different positions, \bar{s}_j , where $j = 1$ to M . We again develop the Schrodinger equation only for the electrons, assuming that the nuclei are at fixed and known positions, i.e., the \bar{s}_j are known and constant. However all N electrons are now attracted to all M nuclei (in principle – though more distant nuclei will tend to be unimportant in practice). So (14) is modified to,

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{j=1}^M \sum_{i=1}^N \frac{Z_j e^2}{4\pi\epsilon_0 |\bar{r}_i - \bar{s}_j|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\bar{r}_i - \bar{r}_j|} \right] \Psi = E\Psi \quad (15)$$

where Z_j is the atomic number of the j^{th} nucleus. This is even nastier than (14) and could not be solved analytically even if the electron-electron term were absent. The solutions to (15) would be, in general, a mixture of atomic orbitals and molecular orbitals.

Ab Initio quantum chemistry is about trying to find decent approximate solutions to (15), possibly for really big molecules like proteins. Even Hartree-Fock methods need to have the full equation (15) carefully simplified before launching into an attempt at numerical solution. I don't know how this is done though, being outside my experience. I would be tempted to say include only the nearest neighbour nuclei, but this would be seriously wrong for, say, pi-electron states in benzene rings – which are delocalised around the whole ring. At this point you need to consult a specialist in molecular modelling.

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