Quantitative treatment of atoms

We will first describe the simplest perturbational and variational calculations of diatomic atoms. The Hamiltonian is

$$H = \sum_{i=1}^{2} \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i^2} \right) + \frac{e^2}{r_{12}}.$$

In the simplest perturbation treatment, the last term (e^2/r_{12}) is taken as the perturbation. The ground state of $H^{(0)}$ is then

$$\psi^{(0)}_{1s1s00} = \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2)\chi_{00}, \quad \chi_{00} = \sqrt{\frac{1}{2}}(\alpha\beta - \beta\alpha),$$

$$E^{(0)}_{1s1s} = 2E_{1s} = -\frac{Z^2e^2}{a_0} = -27.21Z^2 \text{ eV}.$$

Note that $E^{(0)}$ is lower than the real energy of He (-78.98 eV), because a positive term of H is ignored. To first order,

$$E_{1s1s} \approx 2E_{1s} + \langle \psi^{(0)}_{1s1s} | \frac{e^2}{r_{12}} | \psi^{(0)}_{1s1s} \rangle = 2E_{1s} + J_{1s1s} =$$

$$= -\frac{Z^2e^2}{a_0} + \frac{5}{8}\frac{Ze^2}{a_0} = -\frac{Z^2e^2}{a_0}\left(1 - \frac{5}{8}\frac{1}{Z}\right).$$

The table below shows the experimental, zero-order and first-order energies for some light 2-electron species. The last column is obtained by a variational treatment described later.

Energies in eV with minus signs

	Exp.	$E^{(0)}$	$E^{(0)} + E^{(1)}$	Var
He	78.98	108.85	74.83	77.49
Li^+	198.04	244.91	193.89	196.55
Be^{2+}	371.51	435.39	367.36	370.02
B^{3+}	599.43	680.30	595.26	597.92
C^{4+}	881.83	979.63	877.59	880.25

$E^{(0)}$ gives a very large error. This is to be expected, since the perturbation term in the Hamiltonian, e^2/r_{12}, is not much smaller than the potential term in $H^{(0)}$, $-Ze^2/r_{12}$. $E^{(1)}$ corrects a very large part of the error, giving a nearly constant deviation of about 4.15 eV, which is still rather substantial. Note that the relative error of $E^{(0)} + E^{(1)}$ gets smaller with increasing Z, since the perturbation remains the same while the term in $H^{(0)}$ increases in absolute value.

Variational treatment

The important step in applying variational methods is the selection of the trial function. The simplest function for a 2-electron atom is a product of two hydrogenic functions,

$$\phi(\vec{r}_1, \vec{r}_2) = \varphi_{1s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2).$$

The hydrogenic 1s function is $\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$, and we take the same functional with the variational parameter Z' instead of the real Z. We expect Z' to be smaller than Z because of the screening effect.

$$\varphi(r_i) = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} e^{-Z'r/a_0}$$

gives $E'_{1s1s} = \langle\phi|H|\phi\rangle = -\frac{e^2}{a_0}\left(2ZZ' - Z'^2 - \frac{5}{8}Z'\right)$.

Differentiating wrt Z' gives $\frac{dE'}{dZ'} = -\frac{e^2}{a_0}\left(2Z - 2Z' - \frac{5}{8}\right) = 0 \Rightarrow$ $Z' = Z - \frac{5}{16}$,

$$E' = -\frac{Z^2e^2}{a_0}\left(1 - \frac{5}{8}\frac{1}{Z} + \frac{25}{256}\frac{1}{Z^2}\right).$$

The first two terms are similar to those obtained by the perturbation treatment. The results have an error of ~1.5 eV (see table above).

What is the best function (meaning lowest energy) of the form $\phi = \varphi(\vec{r}_1)\varphi(\vec{r}_2)$? It has been shown that the best function corresponds to a physical model, in which the electron "sees" the attraction of the nucleus and the repulsion by the average distribution of the other electron. This potential is

$$V(r_1) = -\frac{Ze^2}{r_1} + e^2 \int \frac{|\varphi(r_2)|^2}{r_{12}} d\vec{r}_2.$$

It is obtained by looking at the repulsion from the electron charge in the volume element $d\vec{r}_2$, which is $\frac{e \cdot e |\varphi(r_2)|^2 d\vec{r}_2}{r_{12}}$. Integration over the $\vec{r}_2$ space gives the expression above. The one-electron Schrödinger equation is then

$$\left[-\frac{\hbar^2}{2m} \nabla_1^2 + V(r_1) \right] = \epsilon_1 \varphi(\vec{r}_1).$$

Note that φ, the solution of this equation, appears also in V, so that the equation must be solved iteratively. This is a simple example of the approximation called self consistent field (SCF) functions, used extensively in quantum chemistry.

Is the SCF function exact? For the He atom it gives a total energy of -77.9 eV, or 1.1 eV above experiment. Why?

The interelectronic interaction taken into account in the SCF model is between average distributions. In real life, the interaction is between instantaneous electron positions. Thus, if one electron is above the nucleus, the other will have larger probability of being below the nucleus. This is the correlation between electrons, which is not allowed for in SCF. The 1.1 eV error in He is the correlation energy of the atom.

The conceptually simplest way to include correlation is to have

r_{12} explicitly in the function. Hylleraas (1928) used the function

$$\phi = Ne^{-\alpha r_1/a_0}e^{-\alpha r_2/a_0}\left(1 + br_{12}\right).$$

The lowest energy was -78.7 eV (0.3 eV off experiment) for $\alpha = 1.849$, $b = 0.364/a_0$. Positive b means higher probability for large r_{12}, as expected. A more complicated function gave an energy off by just 0.01 eV. Pekeris extended this work in 1959, and his final energy was $-2.903724375e^2/a_0$, agreeing with experiment to 9 figures, the experimental accuracy. The calculated ionization potential was 198310.69 cm^{-1}, vs. the experimental 198310.82±0.15. For this kind of accuracy, many small effects had to be included, such as relativistic, magnetic interactions, and others. The success proved that we indeed know the existing interaction terms at least with this accuracy.

A similar calculation for Li (1968) gave a ground state energy of $-7.47802e^2/a_0$, compared with the experimental -7.47807. Unfortunately, the method is not practical for large systems, because the number of r_{ij} variables and the computational effort go up very rapidly.

Many-electron atoms

It is convenient to keep the concept of one-electron orbitals as far as possible, at least as a starting approximation. We can write the trial function as the product

$$\phi = \varphi_1(1)\varphi_2(2)\cdots\varphi_N(N).$$

The potential acting on electron i will include the nuclear attraction and the repulsion by the average distribution of all other electrons, similar to what we used for He

$$V_i(i) = -\frac{Ze^2}{r_i} + \sum_{j\neq i}^{N} e^2 \int \frac{|\varphi_j(j)|^2}{r_{ji}} dj,$$

and the equations will have the form

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V_i(i)\right] \varphi_i(i) = \epsilon_i \varphi_i(i).$$

This is the Hartree method. Note that it is not antisymmetric! One may retain the concept of one-electron orbitals and still have the desired antisymmetry by using a determinantal wavefunction

$$\phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \cdots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \cdots & \varphi_2(N) \\ \cdots & \cdots & \cdots & \cdots \\ \varphi_N(1) & \varphi_N(2) & \cdots & \varphi_N(N) \end{vmatrix}$$

This is the Hartree-Fock, which is used extensively, either in itself or as a starting point for more accurate methods which include correlation. Such methods include, among others

- Configuration interaction, where the wavefunction is a linear combination of many determinants (can go to many millions),

  $$\Phi = \sum_I C_I \phi_I.$$

  It is convenient to start with the Hartree-Fock determinant, then add determinants obtained from it by replacing some occupied orbitals by other orbitals, not occupied in the first determinant.

- Perturbation theory. Highly sophisticated methods have been devised to apply PT in large systems.
- Since perturbation theory often converges slowly, so-called coupled cluster methods sum up important parts of the perturbation to infinite order. These are the most accurate methods known, but also rather expensive.

We will not discuss these methods in detail.