— PY4109 Computational Physics —
Solution of the Radial Schródinger Equation by Finite Difference Method

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I. THE RADIAL SCHRÖDINGER EQUATION

We assume that we have a spherically symmetric atom, so that the potential experienced by an electron at radius r is $V(r)$, depending only on the distance from the origin. The 3-dimensional time-independent Schrödinger equation is then

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(r)\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{1}$$

This equation is separable and the kinetic energy operator can be written in polar coordinates as

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2(r\psi)}{\partial r^2} + \frac{\mathbf{L}^2}{2mr^2}\psi \ , \tag{2}$$

where $\mathbf{L}$ is the angular momentum operator. Assuming that $\psi(\mathbf{r}) = f(r)Y_{lm}(\theta,\phi)$ in spherical polar coordinates, where Y_{lm} is a spherical harmonic function for angular momentum l, and writing $\chi(r) = rf(r)$, we obtain the radial Schrödinger equation for χ:

$$-\frac{d^2\chi}{dr^2} + U(r)\chi(r) = \epsilon\chi(r) \tag{3}$$

where

$$U(r) = \frac{2m}{\hbar^2}V(r) + \frac{l(l+1)}{r^2} \tag{4}$$

and $\epsilon = 2mE/\hbar^2$. To find the bound state energies ($E < 0$), we look for negative eigenvalues ϵ of Eqn. 3 subject to the boundary conditions, $\chi(r) \to 0$ as $r \to 0$ and $r \to \infty$.

II. DEFINING A NON-UNIFORM RADIAL GRID

Because atomic wave functions change much more rapidly near the nucleus ($r = 0$) than at large radius, it is a good idea to concentrate the grid points used in a numerical solution of the differential equation near the origin. In practice, the grid points $r(i)$ are labeled by an integer, $i = 1, 2, \ldots$. A common choice is to define the grid points by

$$r(i) = a[e^{b(i-1)} - 1] \ , \tag{5}$$

where a and b are constants that can be chosen to determine the fineness and spread of the grid. A fortran subroutine to generate this grid is in grid.f in /home/users/PY4109/hartree on the course server, est1.

However, this means the usual radial derivatives need to be expressed in terms of the modified, non-uniform grid. In order to define the appropriate finite difference expressions for first and second derivatives, it is useful to consider i as a continuous, real variable. This allows us to formally re-write radial derivatives in terms of derivatives with respect to i and then use finite difference approximations for those derivatives in terms of the values of the function $\chi_i = \chi(r_i)$ at the radial grid points. Thus,

$$\frac{d(\ldots)}{dr} \equiv \left[\frac{dr}{di}\right]^{-1}\frac{d(\ldots)}{di} \qquad \text{and} \quad \frac{d^2(\ldots)}{dr^2} \equiv \left[\frac{dr}{di}\right]^{-1}\frac{d}{di}\left\{\left[\frac{dr}{di}\right]^{-1}\frac{d(\ldots)}{di}\right\} \tag{6}$$

Taking the finite difference approximation

$$\left[\frac{d\chi}{di}\right]_{i=n+1/2} \approx \chi_{n+1} - \chi_n \ , \tag{7}$$

we get the following finite difference version of Eqn. 3:

$$-\left[\frac{dr}{di}\right]^{-1}_{i=n}\left[\frac{dr}{di}\right]^{-1}_{i=n+1/2}\chi_{n+1}-\left[\frac{dr}{di}\right]^{-1}_{i=n}\left[\frac{dr}{di}\right]^{-1}_{i=n-1/2}\chi_{n-1}+\left[\frac{dr}{di}\right]^{-1}_{i=n}\left\{\left[\frac{dr}{di}\right]^{-1}_{i=n+1/2}+\left[\frac{dr}{di}\right]^{-1}_{i=n-1/2}\right\}\chi_n+U_n\chi_n=\epsilon\chi_n, \tag{8}$$

where $U_n \equiv U(r_n)$, which can be re-written (to 2nd order in the grid separation) as

$$-\left[\frac{dr}{di}\right]^{-1}_{i=n}\left[\frac{dr}{di}\right]^{-1}_{i=n+1/2}\chi_{n+1}-\left[\frac{dr}{di}\right]^{-1}_{i=n}\left[\frac{dr}{di}\right]^{-1}_{i=n-1/2}\chi_{n-1}+2\left[\frac{dr}{di}\right]^{-2}_{i=n}\chi_n+U_n\chi_n=\epsilon\chi_n \tag{9}$$

This equation can be viewed in matrix form as:

$$H_{n,n+1}\chi_{n+1}+H_{n,n-1}\chi_{n-1}+H_{n,n}\chi_n=\epsilon\chi_n \tag{10}$$

where

$$H_{n,n+1}=-\left[\frac{dr}{di}\right]^{-1}_{i=n}\left[\frac{dr}{di}\right]^{-1}_{i=n+1/2} \tag{11}$$

and

$$H_{n,n}=U_n+2\left[\frac{dr}{di}\right]^{-2}_{i=n} \tag{12}$$

We have then reduced the problem of finding ϵ to that of finding the eigenvalues of H.

III. TRANSFORMING THE EQUATION TO HERMITIAN FORM

In the form above, the Hamiltonian H is not Hermitian since $H_{n,n+1} \neq H_{n+1,n}$. However, there is a "natural" transformation that gives the problem in Hermitian form. If we define

$$\chi' = \chi\sqrt{\frac{dr}{di}}\ , \tag{13}$$

then we can rewrite Eqn. 10 as

$$\left[\frac{dr}{di}\right]^{1/2}_{i=n}H_{n,n+1}\left[\frac{dr}{di}\right]^{-1/2}_{i=n+1}\chi'_{n+1}+\left[\frac{dr}{di}\right]^{1/2}_{i=n}H_{n,n-1}\left[\frac{dr}{di}\right]^{-1/2}_{i=n-1}\chi'_{n-1}+H_{n,n}\chi'_n=\epsilon\chi'_n \tag{14}$$

or

$$H'_{n,n+1}\chi'_{n+1}+H'_{n,n-1}\chi'_{n-1}+H'_{n,n}\chi'_n=\epsilon\chi'_n. \tag{15}$$

where

$$H'_{n,n+1}=-\left[\frac{dr}{di}\right]^{-1/2}_{i=n}\left[\frac{dr}{di}\right]^{-1}_{i=n+1/2}\left[\frac{dr}{di}\right]^{-1/2}_{i=n+1}=H'_{n+1,n} \qquad \text{and} \quad H'_{n,n}=H_{n,n}. \tag{16}$$

If the derivatives are only calculated at the grid points, $i = 1, 2, \ldots$, then we can define

$$\left[\frac{dr}{di}\right]^{-1}_{i=n+1/2} \equiv \frac{2}{\left[\frac{dr}{di}\right]_{i=n}+\left[\frac{dr}{di}\right]_{i=n+1}}. \tag{17}$$

Note that the eigenvectors of H' are orthonormal since H' is hermitian. Thus,

$$\sum_{i=1}^{N}\chi_i'^{(j)*}\chi_i'^{(k)}=\delta_{j,k}\ , \tag{18}$$

where $\chi_i'^{(j)}$ is the value of the jth eigenvector at grid point i. For a fine grid, the summation over i can be replaced formally by an integral over i:

$$\int_0^N \chi_i'^{(j)*} \chi_i'^{(k)} di = \delta_{j,k} \ . \tag{19}$$

Using $\chi' = \chi\sqrt{dr/di}$ and $\chi = rf$, we can transform this integral to the form

$$\int_0^{r_N} f^{(j)}(r)^* f^{(k)}(r) r^2 dr = \delta_{j,k} \ , \tag{20}$$

which gives the usual orthonormality condition for eigenstates of the Hamiltonian. Thus, the transformation from χ to χ', given in Eqn. 13, and the transformation $\psi(\mathbf{r}) = r\chi Y_{lm}(\theta,\phi)$, are directly related to the natural integration factor $r^2 dr/di$ for converting integrals with respect to i into the appropriate 3-dimensional integral in spherical polar coordinates; we see that, in order to obtain a hermitian equation for χ', the appropriate scaling factor from χ' to ψ is the square root of the integration factor.

Thus, the contribution from the jth wave function to the charge Q_n inside radius r_n is given by

$$Q_n^{(j)} = \int_0^{r_n} |\psi(r)|^2 r^2 dr \approx \sum_{k=1}^{n} |\chi_k'^{(j)}|^2 \ . \tag{21}$$

This is useful in finding the Hartree potential V_H in the Hartree self-consistent field method, where:

$$V_H(r_n) \ = \ -\int_\infty^{r_n} \frac{Q(r)}{r^2} dr \quad \approx \quad \sum_{i=n}^{N-1} \frac{Q_i}{r_i^2}\frac{dr}{di} + \frac{Q_N}{r_N} \ . \tag{22}$$

Here we are assuming the use of Hartree units, in which the unit of charge is the electronic charge e and the interaction potential between two electrons, separated by a distance r, is $V_{e-e} = 1/r$.

IV. NUMERICAL SOLUTION

If we take a finite (but large) number N of grid points (implicitly setting χ_1' and $\chi_{N+1}' = 0$), then H' is a hermitian matrix of dimension $N-1$, which has non-zero elements only on the diagonal, $i = j$, and immediately above and below the diagonal, $i = j \pm 1$. This type of matrix is called tridiagonal and there are special linear algebra methods developed to find its eigenvalues and eigenvectors [see algol procedure tql2, Num. Math. 11, 293-306 (1968) by Bowdler, Martin, Reinsch and Wilkinson, Handbook for Auto. Comp., Vol. ii – Linear Algebra, 227-240 (1971)]. A standard fortran subroutine for the tql2 algorithm is included in the package eispt.f in /home/users/PY4109/hartree on the course server, est1. A C function for solving the radial Schrödinger equation, which uses the grid generated by grid.f and calls tql2, is in finite_diff.c in the same directory. Note that Hartree units (in which $m = 1$ and $\hbar = 1$) are assumed in these programs, as is standard in atomic physics.