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1 Numerical methods of solving Kohn-Sham equations for atoms

1.1 Units

The Schrödinger-like equations that must be solved take the form

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + e^2\int d^3r'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_{xc}(\mathbf{r})\right)\Psi_\alpha(\mathbf{r}) = E_\alpha\Psi_\alpha(\mathbf{r}), \tag{1}$$

representing the kinetic energy, the electron-nuclear interaction ($V_N(r)$), the Hartree electron-electron interaction ($V_H(\mathbf{r})$), and the exchange-correlation interaction ($V_{xc}(\mathbf{r})$) respectively. In order to express the equations in convenient coordinates, it is convenient to express all distances in units of bohr unit a

$$r = ua \quad \text{where} \quad a \equiv \frac{\hbar^2}{me^2}, \tag{2}$$

where u is a dimensionaless parameters. In practice, in order to simplify the notation in the presentation below, we will use $r \leftrightarrow u$. All energies will be expressed in units of the Rydberg unit $\varepsilon_{\mathrm{Ry}}$

$$\varepsilon_\alpha \equiv E_\alpha/\varepsilon_{\mathrm{Ry}} \quad \text{where} \quad \varepsilon_{\mathrm{Ry}} \equiv \frac{e^2}{2a} = \frac{\hbar^2}{2ma^2}. \tag{3}$$

In these units and notation, the Schrödinger-like equations become

$$\left(-\nabla^2 - \frac{2Z}{r} + v_H(r) + v_{xc}(r)\right)\Psi_\alpha(\mathbf{r}) = \varepsilon_\alpha\Psi_\alpha(\mathbf{r}), \tag{4}$$

where the dimensionaless Hartree potential is given by

$$v_H(r) = V_H(r)/\varepsilon_{\mathrm{Ry}} = 2\int d^3r'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{5}$$

where $v_{xc} \equiv V_{xc}/\varepsilon_{\mathrm{Ry}}$. We can now evaluate the Laplacian operator in spherical polar coordinates and factor the wavefunction into radial and spherical harmonic components

$$\Psi_\alpha(\mathbf{r}) = \frac{\psi_\alpha(r)}{r}Y_{lm}(\hat{\mathbf{r}}). \tag{6}$$

The equation satisfied by the radial function $\psi_\alpha(r)$ takes the form

$$\frac{d^2\psi_\alpha(r)}{dr^2} = A(r)\psi_\alpha(r), \tag{7}$$

where

$$A(r) \equiv \frac{l(l+1)}{r^2} + \frac{2Z}{r} - v_H(r) - v_{xc}(r) + \varepsilon_\alpha. \tag{8}$$

This equation can be solved by various numerical methods. One of the better methods is described below.

1.2 The Numerov method of solving differential equations

One basic approach to developing accurate numerical approximations to the solution of these equations is to use a Taylor's series expansion to relate the behavior of derivatives of your unknown function $f(r)$ to its values at neighboring points of r. Note that for any small distance h,

$$f(r \pm h) = f(r) \pm h\frac{df(r)}{dr} + \frac{h^2}{2!}\frac{d^2f(r)}{dr^2} \pm \frac{h^3}{3!}\frac{d^3f(r)}{dr^3} + \frac{h^4}{4!}\frac{d^4f(r)}{dr^4}\ldots \tag{9}$$

This means that if h is small, we can approximate the second derivative according to

$$\frac{d^2f(r)}{dr^2} \approx \frac{f(r+h)+f(r-h)-2f(r)}{h^2} + O(h^4). \tag{10}$$

By keeping the next even term in the Taylor series expansion, one can derive a Numerov algorithm for this problem. In this case, a higher order approximation to the second derivative is given by

$$\begin{aligned} f(r+h)+&f(r-h)-2f(r) \approx \\ &h^2\frac{d^2f(r)}{dr^2} + \frac{h^2}{12}\left(\frac{d^2f(r+h)}{dr^2} + \frac{d^2f(r-h)}{dr^2} - 2\frac{d^2f(r)}{dr^2}\right) + O(h^6). \end{aligned} \tag{11}$$

The basic equation that defines the Numerov algorithm is as follows:

$$\begin{aligned} &\left(f(r+h) - \frac{h^2}{12}\frac{d^2f(r+h)}{dr^2}\right) + \left(f(r-h) - \frac{h^2}{12}\frac{d^2f(r-h)}{dr^2}\right) \\ &-2\left(f(r) + \frac{5h^2}{12}\frac{d^2f(r)}{dr^2}\right) = 0. \end{aligned} \tag{12}$$

This relation is useful for solving differential equations of the form

$$\frac{d^2f(r)}{dr^2} = A(r)f(r) + B(r), \tag{13}$$

where $f(r)$ is an unknown function and $A(r)$ and $B(r)$ are presumed known.

For a linear radial grid of the form $r_n = r_0 + nh$, the Numerov recursion relation takes the form

$$S(r+h)f(r+h) + S(r-h)f(r-h) + T(r)f(r) = \frac{h^2}{12}\left(B(r+h) + B(r-h) + 10B(r)\right), \tag{14}$$

where

$$S(r) \equiv 1 - \frac{h^2}{12}A(r) \quad \text{and} \quad T(r) \equiv -2 - \frac{10h^2}{12}A(u). \tag{15}$$

Alternatively, it is often convenient to solve these equations using a logarithmic grid of the form

$$r = r_0\left(\mathrm{e}^{nh} - 1\right). \tag{16}$$

In this case, it is convenient to transform the differential equation with the independent variable $u \equiv nh$ to put the equations in a form equivalent to 13. In this case, we can define

$$f(r) \equiv r_0 \mathrm{e}^{u/2} F(u). \tag{17}$$

It can be shown that

$$\frac{d^2 f(r)}{dr^2} = \frac{r_0 \mathrm{e}^{u/2}}{(r+r_0)^2} \left(\frac{d^2 F(u)}{du^2} - \frac{1}{4} F(u) \right). \tag{18}$$

Therefore the equation for the Numerov algorithm is given by

$$\frac{d^2 F(u)}{du^2} = \left((r+r_0)^2 A(u) + \frac{1}{4} \right) F(u) + \frac{(r+r_0)^2}{r_0 \mathrm{e}^{u/2}} B(u) \equiv \widetilde{A}(u) F(u) + \widetilde{B}(u). \tag{19}$$

Once $F(u)$ is determined, the solution $f(r)$ is determined from Eq. (17). Depending on the boundary conditions, the 3-point recursion formula of this algorithm Eq. (14) can be solved as a stepping algorithm or by linear algebra techniques.

For solving the Kohn-Sham equations (Eq. (7)), $B(r) \equiv 0$ and $A(r)$ is given by Eq. (8). In this case, the behavior of the equations for $r \to 0$ needs special attention:

$$\lim_{r \to 0} S(r) f(r) = \begin{cases} -\frac{h^2}{12} 2ZC & \text{for} \quad l = 0 \\ -\frac{h^2}{12} 2C & \text{for} \quad l = 1 \\ 0 & \text{otherwise}, \end{cases} \tag{20}$$

where C is a normalization constant.

For solving for the Hartree potential $v_H(r)$, rather than directly integrating the charge density

$$n(r) = \sum_\alpha w_\alpha \frac{|\psi(r)_\alpha|^2}{4\pi r^2}, \tag{21}$$

it is more accurate to use the Numerov algorithm to solve

$$\frac{d^2 (r v_H(r))}{dr^2} = -8\pi r n(r). \tag{22}$$