



the
abdu salam
international centre for theoretical physics

SMR/1310 - 10

**SPRING COLLEGE ON
NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY**

(7 - 25 May 2001)

"Total energy and Kohn-Sham Hamiltonian of a crystal within DFT"

presented by:

P. GIANNOZZI

Princeton University
Department of Chemistry
Princeton, NJ 08544-1009
U.S.A.

Total energy and Kohn-Sham Hamiltonian of a crystal within DFT

Let us consider a crystal with $N \rightarrow \infty$ unit cells of volume Ω , periodically repeated, with lattice vectors \mathbf{R} . (Pseudo-)Atoms of type μ and ionic charge Z_μ are located at \mathbf{d}_μ in the unit cell. The system contains $N \sum_\mu Z_\mu$ electrons. Its electron states are described by N points \mathbf{k} in the Brillouin Zone. Assuming for simplicity a local electron-ion potential \hat{V}^μ :

$$E_{tot} = E_{kin} + E_{ion-el} + E_{Hartree} + E_{xc} + E_{ion-ion} \quad (1)$$

$$\begin{aligned} &= -\frac{\hbar^2}{2m} \sum_{\mathbf{k},v} \int \psi_{\mathbf{k},v}^*(\mathbf{r}) \nabla^2 \psi_{\mathbf{k},v}(\mathbf{r}) d\mathbf{r} + \sum_{\mathbf{k},v,\mu,\mathbf{R}} \int \psi_{\mathbf{k},v}^*(\mathbf{r}) \hat{V}^\mu(\mathbf{r} - \mathbf{d}_\mu - \mathbf{R}) \psi_{\mathbf{k},v}(\mathbf{r}) d\mathbf{r} \\ &+ \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})] d\mathbf{r} + \frac{e^2}{2} \sum'_{\mu,\nu,\mathbf{R},\mathbf{R}'} \frac{Z_\mu Z_\nu}{|\mathbf{d}_\mu + \mathbf{R} - \mathbf{d}_\nu - \mathbf{R}'|} \end{aligned} \quad (2)$$

where the electron charge density $n(\mathbf{r})$ is given by

$$n(\mathbf{r}) = \sum_{\mathbf{k},v} |\psi_{\mathbf{k},v}(\mathbf{r})|^2 \quad (3)$$

(the sum is over the lowest $\sum_\mu Z_\mu$ occupied states for a semiconductor or insulator, up to the Fermi surface for a metal). Integrals extend on all space. The primed sum appearing in the ion-ion term excludes terms with $\mathbf{d}_\mu + \mathbf{R} - \mathbf{d}_\nu - \mathbf{R}' = 0$.

The Kohn-Sham equation is

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \sum_{\mu,\mathbf{R}} \hat{V}^\mu(\mathbf{r} - \mathbf{d}_\mu - \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \right] \psi_{\mathbf{k},v}(\mathbf{r}) = \epsilon_{\mathbf{k},v} \psi_{\mathbf{k},v}(\mathbf{r}) \quad (4)$$

where the exchange-correlation potential $V_{xc}(\mathbf{r}) = (\delta E_{xc} / \delta n(\mathbf{r}))$. For the LDA case only:

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}, \quad V_{xc}(\mathbf{r}) = \frac{d}{dn} (n \epsilon_{xc}(n))_{n=n(\mathbf{r})} \quad (5)$$

From the Kohn-Sham equation we obtain, by summing over occupied states:

$$\sum_{\mathbf{k},v} \epsilon_{\mathbf{k},v} = -\frac{\hbar^2}{2m} \sum_{\mathbf{k},v} \int \psi_{\mathbf{k},v}^*(\mathbf{r}) \nabla^2 \psi_{\mathbf{k},v}(\mathbf{r}) d\mathbf{r} + \sum_{\mathbf{k},v,\mu,\mathbf{R}} \int \psi_{\mathbf{k},v}^*(\mathbf{r}) \hat{V}^\mu(\mathbf{r} - \mathbf{d}_\mu - \mathbf{R}) \psi_{\mathbf{k},v}(\mathbf{r}) d\mathbf{r} + e^2 \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int n(\mathbf{r}) V_{xc}(\mathbf{r}) d\mathbf{r} \quad (6)$$

and we can give an alternate formula for the total energy of a crystal:

$$E_{tot} = \sum_{\mathbf{k},v} \epsilon_{\mathbf{k},v} - \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int n(\mathbf{r}) (\epsilon_{xc}(\mathbf{r}) - V_{xc}(\mathbf{r})) d\mathbf{r} + \frac{e^2}{2} \sum'_{\mu,\nu,\mathbf{R},\mathbf{R}'} \frac{Z_\mu Z_\nu}{|\mathbf{d}_\mu + \mathbf{R} - \mathbf{d}_\nu - \mathbf{R}'|} \quad (7)$$

Plane-wave – Pseudopotential formalism

Let us consider the \mathbf{G} -space representation of the wavefunctions:

$$|\psi_{\mathbf{k}}\rangle = \sum_{\mathbf{G}} \Psi(\mathbf{k} + \mathbf{G}) |\mathbf{k} + \mathbf{G}\rangle, \quad \Psi(\mathbf{k} + \mathbf{G}) = \langle \mathbf{k} + \mathbf{G} | \psi_{\mathbf{k}} \rangle, \quad |\mathbf{k} + \mathbf{G}\rangle = \frac{1}{\sqrt{V}} e^{i(\mathbf{k} + \mathbf{G})\mathbf{r}}, \quad (8)$$

where $V = N\Omega$ is the volume of the crystal. With these definitions, the normalizations are:

$$\langle \mathbf{k} + \mathbf{G} | \mathbf{k} + \mathbf{G} \rangle = \delta_{\mathbf{G},\mathbf{G}'}, \quad \langle \psi_{\mathbf{k}} | \psi_{\mathbf{k}} \rangle = 1 \quad \text{if} \quad \sum_{\mathbf{G}} |\Psi(\mathbf{k} + \mathbf{G})|^2 = 1. \quad (9)$$

Let us define the Fourier transform for a periodic function $F(\mathbf{r}) = \sum_{\mathbf{R}} f(\mathbf{r} - \mathbf{R})$ as:

$$F(\mathbf{G}) = \frac{1}{N\Omega} \int d\mathbf{r} F(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}} = \frac{1}{\Omega} \int d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}} = \langle \mathbf{k} + \mathbf{G}_1 | F(\mathbf{r}) | \mathbf{k} + \mathbf{G}_2 \rangle, \quad \mathbf{G} = \mathbf{G}_1 - \mathbf{G}_2 \quad (10)$$

$$F(\mathbf{r}) = \sum_{\mathbf{G}} F(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}. \quad (11)$$

We assume non local pseudopotential of general form $\hat{V}^\mu = V_\mu(r) + \sum_i V_{\mu,i}(\mathbf{r}, \mathbf{r}')$. The total energy per unit cell in reciprocal space is:

$$\begin{aligned} \frac{E_{tot}}{N} &= \frac{1}{N} \frac{\hbar^2}{2m} \sum_{\mathbf{k},v} \sum_{\mathbf{G}} |\Psi_v(\mathbf{k} + \mathbf{G})|^2 (\mathbf{k} + \mathbf{G})^2 + \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) \sum_{\mu} S_\mu(\mathbf{G}) V_\mu(\mathbf{G}) + \frac{1}{N} \sum_{\mathbf{k},v} \sum_{\mu,i} \sum_{\mathbf{G},\mathbf{G}'} S_\mu(\mathbf{G} - \mathbf{G}') \times \\ &\times \Psi_v^*(\mathbf{k} + \mathbf{G}) \Psi_v(\mathbf{k} + \mathbf{G}') V_{\mu,i}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') + \frac{\Omega}{2} \sum_{\mathbf{G}} n^*(\mathbf{G}) V_{Hartree}(\mathbf{G}) + \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) \epsilon_{xc}(\mathbf{G}) + \frac{e^2}{2} \sum'_{\mu,\nu,\mathbf{R}} \frac{Z_\mu Z_\nu}{|\mathbf{d}_\mu - \mathbf{d}_\nu - \mathbf{R}|} \end{aligned} \quad (12)$$

where $S_\mu(\mathbf{G}) = \sum_{\mathbf{d}_\mu} e^{-i\mathbf{G}\mathbf{d}_\mu}$ is the structure factor, and

$$V_{Hartree}(\mathbf{G}) = 4\pi e^2 \frac{n(\mathbf{G})}{\mathbf{G}^2}, \quad V_\mu(\mathbf{G}) = \frac{1}{\Omega} \int V_\mu(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}} d\mathbf{r}, \quad V_{\mu,i}(\mathbf{k}_1, \mathbf{k}_2) = \frac{1}{\Omega} \int e^{-i\mathbf{k}_1\mathbf{r}} V_{\mu,i}(\mathbf{r}, \mathbf{r}') e^{i\mathbf{k}_2\mathbf{r}'} d\mathbf{r}d\mathbf{r}'. \quad (13)$$

Note that we have assumed one atom of each kind. The generalization is straightforward: the structure factor becomes $S_\mu(\mathbf{G}) = \sum_{i_\mu} e^{-i\mathbf{G}\mathbf{d}_{i_\mu}}$ where i_μ runs over atoms of the same kind μ .

Using eigenvalues sum, the total energy per unit cell is

$$\frac{E_{tot}}{N} = \frac{1}{N} \sum_{\mathbf{k},v} \epsilon_{\mathbf{k},v} - \frac{\Omega}{2} \sum_{\mathbf{G}} n^*(\mathbf{G}) V_{Hartree}(\mathbf{G}) + \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) (\epsilon_{xc}(\mathbf{G}) - V_{xc}(\mathbf{G})) + \frac{e^2}{2} \sum_{\mu,\nu,\mathbf{R}} \frac{Z_\mu Z_\nu}{|\mathbf{d}_\mu - \mathbf{d}_\nu - \mathbf{R}|}. \quad (14)$$

In the plane-wave representation the Kohn-Sham equation becomes

$$\sum_{\mathbf{G}'} \langle \mathbf{k} + \mathbf{G} | H - \epsilon | \mathbf{k} + \mathbf{G}' \rangle \Psi(\mathbf{k} + \mathbf{G}') = 0, \quad \text{or} \quad \sum_{\mathbf{G}'} \langle \mathbf{k} + \mathbf{G} | H | \mathbf{k} + \mathbf{G}' \rangle \Psi(\mathbf{k} + \mathbf{G}') = \epsilon \Psi(\mathbf{k} + \mathbf{G}) \quad (15)$$

The matrix elements of the hamiltonian are

$$\begin{aligned} \langle \mathbf{k} + \mathbf{G} | H - \epsilon | \mathbf{k} + \mathbf{G}' \rangle &= \left(-\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2 - \epsilon \right) \delta_{\mathbf{G}\mathbf{G}'} + \sum_{\mu} S_\mu(\mathbf{G} - \mathbf{G}') \left(V_\mu(\mathbf{G} - \mathbf{G}') + \sum_l V_{\mu,l}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') \right) \\ &+ V_{Hartree}(\mathbf{G} - \mathbf{G}') + V_{xc}(\mathbf{G} - \mathbf{G}'). \end{aligned} \quad (16)$$

Divergent Terms in the potential

The Hartree term, $V_{Hartree}(0)$, and local potential term, $\sum_{\mu} S_\mu(0) V_\mu(0)$, are separately divergent and must be treated in a special way. Let us consider their sum $\tilde{V}(\mathbf{r}) = V_{loc}(\mathbf{r}) + V_{Hartree}(\mathbf{r})$. Its $\mathbf{G} = 0$ term is not divergent:

$$\tilde{V}(\mathbf{G} = 0) = \frac{1}{\Omega} \int d\mathbf{r} \left(\sum_{\mu} V_\mu(\mathbf{r} - \mathbf{d}_\mu) + \frac{1}{N} e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) = \frac{1}{\Omega} \sum_{\mu} \int d\mathbf{r} \left(V_\mu(r) + \frac{Z_\mu e^2}{r} \right) = \frac{1}{\Omega} \sum_{\mu} \alpha_\mu \quad (17)$$

where we used

$$V_\mu(r) \sim -\frac{Z_\mu e^2}{r} \quad \text{for large } r, \quad \frac{1}{N} \int n(\mathbf{r}) = \sum_{\mu} Z_\mu. \quad (18)$$

The α_μ are parameters depending only on the pseudopotential.

Divergent Terms in the energy

The $\mathbf{G} = 0$ terms of the ion-ion, Hartree, and local pseudopotential terms in the total energy are separately divergent and must be treated in a special way. Let us call E_{div} the sum of all divergent terms.

First Step: split $E_{div} = E_{div}^{(1)} + E_{div}^{(2)}$, with

$$E_{div}^{(1)} = \int n(\mathbf{r}) \sum_{\mu} V_{\mu}(\mathbf{r} - \mathbf{d}_{\mu}) d\mathbf{r} + \frac{1}{N} e^2 \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (19)$$

$$E_{div}^{(2)} = \frac{e^2}{2} \sum'_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu}Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} - \frac{1}{N} \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (20)$$

The first divergent term can be written as

$$E_{div}^{(1)} = \int n(\mathbf{r}) \tilde{V}(\mathbf{r}) d\mathbf{r}. \quad (21)$$

The $\mathbf{G} = 0$ term of $\tilde{V}(\mathbf{G})$ is not divergent and has been previously calculated:

$$\tilde{V}(\mathbf{G} = 0) = \frac{1}{\Omega} \sum_{\mu} \alpha_{\mu}, \quad n(\mathbf{G} = 0) = \sum_{\mu} \frac{Z_{\mu}}{\Omega}. \quad (22)$$

We finally get for the $\mathbf{G} = 0$ contribution what is usually called “ αZ term”:

$$E_{div}^{(1)} = \Omega \sum_{\mathbf{G} \neq 0} n^*(\mathbf{G}) \tilde{V}(\mathbf{G}) + \frac{1}{\Omega} (\sum_{\mu} Z_{\mu}) (\sum_{\mu} \alpha_{\mu}) \quad (23)$$

Second step: write $E_{div}^{(2)} = E_{Ewald}^{(1)} + E_{Ewald}^{(2)} - E_{Hartree}$, with

$$E_{Ewald}^{(1)} = \frac{e^2}{2} \sum'_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu}Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \operatorname{erfc}(\sqrt{\eta}|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|), \quad E_{Ewald}^{(2)} = \frac{e^2}{2} \sum_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu}Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \operatorname{erf}(\sqrt{\eta}|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|) - e^2 \sqrt{\frac{\eta}{\pi}} \sum_{\mu} Z_{\mu}^2. \quad (24)$$

This identity is verified for any value of η . The sum in $E_{Ewald}^{(2)}$ includes the term with $\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R} = 0$ (note the missing prime), that is subtracted back in the second term of $E_{Ewald}^{(2)}$ (note that $\operatorname{erf}(x) \rightarrow 2x/\sqrt{\pi}$ for small x).

The first Ewald term $E_{Ewald}^{(1)}$ is rapidly convergent in real space for any reasonable values of η .

The sum in $E_{Ewald}^{(2)}$ can be written as the interaction energy between point charges $\tilde{n}(\mathbf{r})$ and the potential $\Phi(\mathbf{r})$ produced by a gaussian distribution of charges:

$$E_{Ewald}^{(2)} = \int \tilde{n}(\mathbf{r})\Phi(\mathbf{r})d\mathbf{r} - e^2\sqrt{\frac{\eta}{\pi}}\sum_{\mu}Z_{\mu}^2, \quad \tilde{n}(\mathbf{r}) = \sum_{\mu}Z_{\mu}\delta(\mathbf{r} - \mathbf{d}_{\mu}), \quad \Phi(\mathbf{r}) = \frac{e^2}{2}\sum_{\mu,\mathbf{R}}\frac{Z_{\mu}\text{erf}(\sqrt{\eta}|\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|} \quad (25)$$

In reciprocal space, by using the Fourier transform

$$\frac{1}{r'}\text{erf}(\sqrt{\eta}r') = \left(\frac{\eta}{\pi}\right)^{3/2}\int\frac{e^{-\eta r^2}}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r} = \int\frac{4\pi e^{-G^2/4\eta}}{G^2}e^{i\mathbf{G}\cdot\mathbf{r}'}d\mathbf{G} \quad (26)$$

one obtains

$$E_{Ewald}^{(2)} = \Omega\sum_{\mathbf{G}}\tilde{n}^*(\mathbf{G})\Phi(\mathbf{G}) - e^2\sqrt{\frac{\eta}{\pi}}\sum_{\mu}Z_{\mu}^2, \quad \tilde{n}(\mathbf{G}) = \sum_{\mu}Z_{\mu}e^{i\mathbf{G}\cdot\mathbf{d}_{\mu}}, \quad \Phi(\mathbf{G}) = \frac{4\pi}{\Omega}\frac{e^2}{2}\sum_{\mu}Z_{\mu}e^{i\mathbf{G}\cdot\mathbf{d}_{\mu}}\frac{e^{-G^2/4\eta}}{G^2} \quad (27)$$

The $\mathbf{G} = 0$ contribution to $E_{Ewald}^{(2)} - E_{Hartree}$:

$$E_0 = \Omega\left(n(0)\Phi(0) - \frac{1}{2}\tilde{n}(0)V_{Hartree}(0)\right) \quad (28)$$

is no longer divergent, because $n(0) = \tilde{n}(0) = \sum_{\mu}Z_{\mu}/\Omega$ due to the neutrality of the system:

$$\begin{aligned} (\Phi - V_{Hartree})(\mathbf{G} = 0) &= \frac{e^2}{2}\frac{1}{N\Omega}\int\left(\sum_{\mu,\mathbf{R}}Z_{\mu}\frac{\text{erf}(\sqrt{\eta}|\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|} - \int\frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}'\right)d\mathbf{r} \\ &= \frac{e^2}{2}\frac{1}{\Omega}\left(\sum_{\mu}Z_{\mu}\right)\int\frac{\text{erf}(\sqrt{\eta}r) - 1}{r}dr \end{aligned} \quad (29)$$

The integral appearing in the last expression can be found in tables:

$$\int\frac{\text{erf}(\sqrt{\eta}r) - 1}{r}dr = 4\pi\int(\text{erf}(\sqrt{\eta}r) - 1)rdr = 4\pi\frac{1}{4\eta}. \quad (30)$$

Putting all pieces together, one obtains for $E_{div}^{(2)}$:

$$\begin{aligned}
E_{div}^{(2)} = & -\frac{\Omega}{2} \sum_{\mathbf{G}} n^*(\mathbf{G}) V_{Hartree}(\mathbf{G}) + \frac{4\pi}{\Omega} \frac{e^2}{2} \sum_{\mathbf{G} \neq 0} \left| \sum_{\mu} Z_{\mu} e^{i\mathbf{G}\mathbf{d}_{\mu}} \right|^2 \frac{e^{-G^2/4\eta}}{G^2} \\
& + \frac{e^2}{2} \sum'_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu} Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \text{erfc}(\sqrt{\eta} |\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|) - e^2 \sqrt{\frac{\eta}{\pi}} \sum_{\mu} Z_{\mu}^2 - \frac{4\pi}{\Omega} \frac{e^2}{2} \frac{1}{4\eta} \left(\sum_{\mu} Z_{\mu} \right)^2
\end{aligned} \tag{31}$$

and for the total energy:

$$\begin{aligned}
\frac{E_{tot}}{N} = & \frac{1}{N} \frac{\hbar^2}{2m} \sum_{\mathbf{k}, \nu} \sum_{\mathbf{G}} |\Psi_{\nu}(\mathbf{k} + \mathbf{G})|^2 (\mathbf{k} + \mathbf{G})^2 + \frac{1}{N} \sum_{\mathbf{k}, \nu} \sum_{\mu, i} \sum_{\mathbf{G}, \mathbf{G}'} S_{\mu}(\mathbf{G} - \mathbf{G}') \Psi_{\nu}^*(\mathbf{k} + \mathbf{G}) \Psi_{\nu}(\mathbf{k} + \mathbf{G}') V_{\mu, i}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') \\
& + \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) \epsilon_{xc}(\mathbf{G}) + E_{div}^{(1)} + E_{div}^{(2)}.
\end{aligned} \tag{32}$$

If the sum of the eigenvalues is used, $E_{div}^{(1)}$ is already calculated in the sum of eigenvalues, and the total energy becomes:

$$\frac{E_{tot}}{N} = \frac{1}{N} \sum_{\mathbf{k}, \nu} \epsilon_{\mathbf{k}, \nu} + \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) (\epsilon_{xc}(\mathbf{G}) - V_{xc}(\mathbf{G})) + E_{div}^{(2)}. \tag{33}$$