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

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

Let us consider a crystal with $N \to \infty$ 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 $\mathbf{d}_\mu$ 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 $\hat{V}^\mu$:

$$E_{tot} = E_{kin} + E_{ion-el} + E_{Hartree} + E_{xc} + E_{ion-ion} \tag{1}$$

$$= -\frac{\hbar^2}{2m} \sum_{\mathbf{k},v} \int \psi^*_{\mathbf{k},v}(\mathbf{r}) \nabla^2 \psi_{\mathbf{k},v}(\mathbf{r}) d\mathbf{r} + \sum_{\mathbf{k},v,\mu,\mathbf{R}} \int \psi^*_{\mathbf{k},v}(\mathbf{r}) \hat{V}^\mu(\mathbf{r} - \mathbf{d}_\mu - \mathbf{R}) \psi_{\mathbf{k},v}(\mathbf{r}) d\mathbf{r}$$
$$+ \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} d\mathbf{r} d\mathbf{r}' + \int n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})] d\mathbf{r} + \frac{e^2}{2} {\sum_{\mu,\nu,\mathbf{R},\mathbf{R}'}}' \frac{Z_\mu Z_\nu}{\mid \mathbf{d}_\mu + \mathbf{R} - \mathbf{d}_\nu - \mathbf{R}' \mid} \tag{2}$$

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

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

(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

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

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

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

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

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

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

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

Plane-wave – Pseudopotential formalism

Let us consider the **G**-space representation of the wavefunctions:

$$|\psi_{\mathbf{k}}> = \sum_{\mathbf{G}} \Psi(\mathbf{k}+\mathbf{G})|\mathbf{k}+\mathbf{G}>, \qquad \Psi(\mathbf{k}+\mathbf{G}) = <\mathbf{k}+\mathbf{G} \mid \psi_{\mathbf{k}}>, \qquad \mid \mathbf{k}+\mathbf{G}> = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \tag{8}$$

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

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

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

$$F(\mathbf{G}) = \frac{1}{N\Omega}\int d\mathbf{r} F(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}} = \frac{1}{\Omega}\int d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}} = <\mathbf{k}+\mathbf{G}_1 \mid F(\mathbf{r}) \mid \mathbf{k}+\mathbf{G}_2> \ , \qquad \mathbf{G} = \mathbf{G}_1 - \mathbf{G}_2 \tag{10}$$

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

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:

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

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

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

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

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

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

$$\sum_{\mathbf{G}'} < \mathbf{k}+\mathbf{G} \mid H - \epsilon \mid \mathbf{k}+\mathbf{G}' > \Psi(\mathbf{k}+\mathbf{G}') = 0, \qquad \text{or} \qquad \sum_{\mathbf{G}'} < \mathbf{k}+\mathbf{G} \mid H \mid \mathbf{k}+\mathbf{G}' > \Psi(\mathbf{k}+\mathbf{G}') = \epsilon\Psi(\mathbf{k}+\mathbf{G}) \tag{15}$$

The matrix elements of the hamiltonian are

$$\begin{aligned} < \mathbf{k}+\mathbf{G} \mid H - \epsilon \mid \mathbf{k}+\mathbf{G}' > \;&=\; \Big(-\frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2 - \epsilon\Big)\delta_{\mathbf{G}\mathbf{G}'} + \sum_\mu S_\mu(\mathbf{G}-\mathbf{G}')\Big(V_\mu(\mathbf{G}-\mathbf{G}') + \sum_l V_{\mu,l}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}')\Big) \\ &+\; V_{Hartree}(\mathbf{G}-\mathbf{G}') + V_{xc}(\mathbf{G}-\mathbf{G}'). \end{aligned} \tag{16}$$

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:

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

where we used

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

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 $E_{div} = E^{(1)}_{div} + E^{(2)}_{div}$, with

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

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

The first divergent term can be written as

$$E^{(1)}_{div} = \int n(\mathbf{r}) \tilde{V}(\mathbf{r}) d\mathbf{r}. \tag{21}$$

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

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

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

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

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

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

This identity is verified for any value of η. The sum in $E^{(2)}_{Ewald}$ 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 $E^{(2)}_{Ewald}$ (note that $\mathrm{erf}(x) \to 2x/\sqrt{\pi}$ for small x).

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

The sum in $E^{(2)}_{Ewald}$ 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:

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

In reciprocal space, by using the Fourier transform

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

one obtains

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

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

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

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

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

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

$$\int\frac{\mathrm{erf}(\sqrt{\eta}r)-1}{r}d\mathbf{r} = 4\pi\int(\mathrm{erf}(\sqrt{\eta}r)-1)rdr = 4\pi\frac{1}{4\eta}. \tag{30}$$

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

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

and for the total energy:

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

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

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