

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

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

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

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

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

Using the previous definition of $\tilde{V}(\mathbf{r})$, 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”:

$$E_{div}^{(1)} = \Omega \sum_{\mathbf{G} \neq 0} n^*(\mathbf{G}) \tilde{V}(\mathbf{G}) + \frac{1}{\Omega} (\sum_{\mu} Z_{\mu}) (\sum_{\mu} \alpha_{\mu}) = \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) \tilde{V}_{loc}(\mathbf{G}) + 2\tilde{E}_{Hartree} \quad (23)$$

where \tilde{V}_{loc} is the local potential for $\mathbf{G} \neq 0$, contains the αZ term in $\mathbf{G} = 0$ component, and

$$\tilde{E}_{Hartree} = \frac{\Omega}{2} \sum_{\mathbf{G} \neq 0} n^*(\mathbf{G}) V_{Hartree}(\mathbf{G}). \quad (24)$$

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

$$E_{Ewald}^{(1)} = \frac{e^2}{2} \sum'_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu}Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \operatorname{erfc}(\sqrt{\eta}|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|), \quad E_{Ewald}^{(2)} = \frac{e^2}{2} \sum_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu}Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \operatorname{erf}(\sqrt{\eta}|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|) - e^2 \sqrt{\frac{\eta}{\pi}} \sum_{\mu} Z_{\mu}^2. \quad (25)$$

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 $n_c(\mathbf{r})$ and the potential $V_g(\mathbf{r})$ produced by a gaussian distribution of charges:

$$E_{Ewald}^{(2)} = \frac{1}{2} \int n_c(\mathbf{r}) V_g(\mathbf{r}) d\mathbf{r} - e^2 \sqrt{\frac{\eta}{\pi}} \sum_{\mu} Z_{\mu}^2, \quad n_c(\mathbf{r}) = \sum_{\mu} Z_{\mu} \delta(\mathbf{r} - \mathbf{d}_{\mu}), \quad V_g(\mathbf{r}) = e^2 \sum_{\mu, \mathbf{R}} \frac{Z_{\mu} \text{erf}(\sqrt{\eta} |\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|} \quad (26)$$

In reciprocal space, by using the Fourier transform

$$\frac{1}{r'} \text{erf}(\sqrt{\eta} r') = \left(\frac{\eta}{\pi}\right)^{3/2} \int \frac{e^{-\eta r^2}}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} = \int \frac{4\pi e^{-G^2/4\eta}}{G^2} e^{i\mathbf{G} \cdot \mathbf{r}'} d\mathbf{G} \quad (27)$$

one obtains (forgetting for the moment the divergence of $V_g(\mathbf{G} = 0)$):

$$E_{Ewald}^{(2)} = \frac{\Omega}{2} \sum_{\mathbf{G}} n_c^*(\mathbf{G}) V_g(\mathbf{G}) - e^2 \sqrt{\frac{\eta}{\pi}} \sum_{\mu} Z_{\mu}^2, \quad n_c(\mathbf{G}) = \frac{1}{\Omega} \sum_{\mu} Z_{\mu} e^{i\mathbf{G} \cdot \mathbf{d}_{\mu}}, \quad V_g(\mathbf{G}) = \frac{4\pi e^2}{\Omega} \sum_{\mu} Z_{\mu} e^{i\mathbf{G} \cdot \mathbf{d}_{\mu}} \frac{e^{-G^2/4\eta}}{G^2} \quad (28)$$

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

$$E_0 = \frac{\Omega}{2} (n_c(0) V_g(0) - n(0) V_{Hartree}(0)) \quad (29)$$

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

$$\begin{aligned} (V_g - V_{Hartree})(\mathbf{G} = 0) &= \frac{e^2}{N\Omega} \int \left(\sum_{\mu, \mathbf{R}} Z_{\mu} \frac{\text{erf}(\sqrt{\eta} |\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|} - \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) d\mathbf{r} \\ &= \frac{e^2}{\Omega} \left(\sum_{\mu} Z_{\mu} \right) \int \frac{\text{erf}(\sqrt{\eta} r) - 1}{r} d\mathbf{r} = \frac{e^2}{\Omega} \left(\sum_{\mu} Z_{\mu} \right) \frac{\pi}{\eta} \end{aligned} \quad (30)$$

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

$$\int \frac{\text{erf}(\sqrt{\eta} r) - 1}{r} d\mathbf{r} = 4\pi \int (\text{erf}(\sqrt{\eta} r) - 1) r dr = 4\pi \frac{1}{4\eta}. \quad (31)$$

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

$$\begin{aligned} E_{div}^{(2)} = -\tilde{E}_{hartree} + E_{Ewald} &= -\frac{\Omega}{2} \sum_{\mathbf{G} \neq 0} n^*(\mathbf{G}) V_{Hartree}(\mathbf{G}) + \frac{4\pi e^2}{\Omega} \frac{1}{2} \sum_{\mathbf{G} \neq 0} \left| \sum_{\mu} Z_{\mu} e^{i\mathbf{G} \cdot \mathbf{d}_{\mu}} \right|^2 \frac{e^{-G^2/4\eta}}{G^2} \\ &+ \frac{e^2}{2} \sum_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu} Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \text{erfc}(\sqrt{\eta} |\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|) - e^2 \sqrt{\frac{\eta}{\pi}} \sum_{\mu} Z_{\mu}^2 - \frac{4\pi e^2}{\Omega} \frac{1}{2} \frac{1}{4\eta} \left(\sum_{\mu} Z_{\mu} \right)^2 \end{aligned} \quad (32)$$

and for the total energy:

$$\begin{aligned} \frac{E_{tot}}{N} &= \frac{1}{N} \frac{\hbar^2}{2m} \sum_{\mathbf{k},v} \sum_{\mathbf{G}} |\Psi_v(\mathbf{k} + \mathbf{G})|^2 (\mathbf{k} + \mathbf{G})^2 + \frac{1}{N} \sum_{\mathbf{k},v} \sum_{\mu,i} \sum_{\mathbf{G},\mathbf{G}'} S_\mu(\mathbf{G} - \mathbf{G}') \Psi_v^*(\mathbf{k} + \mathbf{G}) \Psi_v(\mathbf{k} + \mathbf{G}') V_{\mu,i}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') \\ &+ \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) \epsilon_{xc}(\mathbf{G}) + \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) \tilde{V}_{loc}(\mathbf{G}) + \tilde{E}_{Hartree} + E_{Ewald}. \end{aligned} \quad (33)$$

One can use the sum of the eigenvalues to calculate the total energy: the kinetic, non local, and local (including the αZ term) contributions disappear and the expression of the total energy becomes:

$$\frac{E_{tot}}{N} = \frac{1}{N} \sum_{\mathbf{k},v} \epsilon_{\mathbf{k},v} + \Omega \sum_{\mathbf{G}} n^*(\mathbf{G}) (\epsilon_{xc}(\mathbf{G}) - V_{xc}(\mathbf{G})) - \tilde{E}_{Hartree} + E_{Ewald}. \quad (34)$$

Calculation of energy in CP

Let us define n_g as the sum of gaussian charges centered at atomic sites:

$$n_g(\mathbf{r}) = \sum_{\mu} Z_{\mu} \left(\frac{\eta}{\pi} \right)^{3/2} e^{-\eta(\mathbf{r} - \mathbf{d}_{\mu})^2}. \quad (35)$$

The divergent terms E_{div} of the energy can be rewritten as $E_{div} = E_{div}^{(1)} + E_{div}^{(2)}$, with

$$E_{div}^{(1)} = \int n(\mathbf{r}) \sum_{\mu} V_{\mu}(\mathbf{r} - \mathbf{d}_{\mu}) d\mathbf{r} - \frac{1}{N} e^2 \int \frac{n(\mathbf{r}) n_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (36)$$

$$E_{div}^{(2)} = \frac{e^2}{2} \sum_{\mu,\nu,\mathbf{R}}' \frac{Z_{\mu} Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} + \frac{1}{N} \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{N} e^2 \int \frac{n(\mathbf{r}) n_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (37)$$

$E_{div}^{(1)}$ can be rewritten as

$$E_{div}^{(1)} = \int n(\mathbf{r}) V_{loc+g}(\mathbf{r}) d\mathbf{r}, \quad V_{loc+g}(\mathbf{r}) = \left(\sum_{\mu} V_{\mu}(\mathbf{r} - \mathbf{d}_{\mu}) + V_g(\mathbf{r}) \right), \quad (38)$$

where $V_g(\mathbf{r})$ is the potential generated by the gaussians. The singularity at $\mathbf{G} = 0$ disappears :

$$V_{loc+g}(\mathbf{G} = 0) = \frac{1}{\Omega} \sum_{\mu} \int d\mathbf{r} \left(V_{\mu}(r) + \frac{Z_{\mu} e^2 \text{erf}(\sqrt{\eta} r)}{r} \right) \equiv \frac{1}{\Omega} \sum_{\mu} \alpha'_{\mu}. \quad (39)$$

Note that this term is similar to, but not equal to, the αZ term. $E_{div}^{(1)}$ can be rewritten as:

$$E_{div}^{(1)} = \frac{1}{\Omega} \left(\sum_{\mu} Z_{\mu} \right) \left(\sum_{\mu} \alpha'_{\mu} \right) + \Omega \sum_{\mathbf{G} \neq 0} n^*(\mathbf{G}) V_{loc+g}(\mathbf{G}). \quad (40)$$

$E_{div}^{(2)}$ can be rewritten as $E_{div}^{(2)} = E_{Ewald} + E_{H+g}$, where E_{Ewald} is the well-known Ewald sum,

$$E_{Ewald} = \frac{e^2}{2} \sum'_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu} Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} - \frac{1}{N} \frac{e^2}{2} \int \frac{n_g(\mathbf{r}) n_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (41)$$

while E_{H+g} is the electrostatic energy of a system of electrons and ions with a gaussian charge distribution:

$$E_{H+g} = \frac{1}{N} \frac{e^2}{2} \int \frac{(n(\mathbf{r}) + n_g(\mathbf{r}))(n(\mathbf{r}') + n_g(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (42)$$

Both terms are regular at $\mathbf{G} = 0$ because they are the electrostatic energy of neutral systems. E_{H+g} can be directly calculated:

$$E_{H+g} = \Omega \sum_{\mathbf{G} \neq 0} (n^*(\mathbf{G}) + n_g^*(\mathbf{G})) V_{H+g}(\mathbf{G}), \quad V_{H+g}(\mathbf{G}) = \frac{4\pi e^2}{G^2} (n(\mathbf{G}) + n_g(\mathbf{G})). \quad (43)$$

E_{Ewald} can be easily computed using the same technique used before:

$$E_{Ewald} = E_{Ewald}^{(1)} + E_{Ewald}^{(2)}, \quad (44)$$

where (note the sum over all vectors including $\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R} = 0$):

$$E_{Ewald}^{(1)} = \frac{e^2}{2} \sum'_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu} Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \text{erf}(\sqrt{\zeta} |\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|) - \frac{1}{N} \frac{e^2}{2} \int \frac{n_g(\mathbf{r}) n_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (45)$$

and (note the self-interaction term compensating the $\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R} = 0$ contribution of the former term):

$$E_{Ewald}^{(2)} = \frac{e^2}{2} \sum'_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu} Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \text{erfc}(\sqrt{\zeta} |\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|) - e^2 \sqrt{\frac{\zeta}{\pi}} \sum_{\mu} Z_{\mu}^2. \quad (46)$$

for an arbitrary value of ζ . $E_{Ewald}^{(1)}$ can be made to vanish, because both terms appearing in it can be written in reciprocal space as an Ewald sum. Leaving apart the $\mathbf{G} = 0$ contribution,

$$\frac{1}{N} \frac{e^2}{2} \int \frac{n_g(\mathbf{r}) n_g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \frac{\Omega}{2} \sum_{\mathbf{G} \neq 0} n_g^*(\mathbf{G}) V_g(\mathbf{G}) = \frac{4\pi e^2}{\Omega} \frac{e^2}{2} \sum_{\mathbf{G} \neq 0} \left| \sum_{\mu} Z_{\mu} e^{i\mathbf{G} \cdot \mathbf{d}_{\mu}} \right|^2 \frac{e^{-G^2/2\eta}}{G^2}. \quad (47)$$

This expression comes from the Fourier transform of $n_g(\mathbf{r})$ and $V_g(\mathbf{r})$:

$$n_g(\mathbf{G}) = \frac{1}{\Omega} \sum_{\mu} Z_{\mu} e^{i\mathbf{G} \cdot \mathbf{d}_{\mu}} e^{-G^2/4\eta}, \quad V_g(\mathbf{G}) = \frac{4\pi e^2 n_g(\mathbf{G})}{G^2}. \quad (48)$$

By setting $2\zeta = \eta$, one finds exactly the reciprocal space expression for the first term:

$$\frac{e^2}{2} \sum_{\mu, \nu, \mathbf{R}} \frac{Z_{\mu} Z_{\nu}}{|\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|} \text{erf}(\sqrt{\zeta} |\mathbf{d}_{\mu} - \mathbf{d}_{\nu} - \mathbf{R}|) = \frac{4\pi e^2}{\Omega} \frac{1}{2} \sum_{\mathbf{G} \neq 0} \left| \sum_{\mu} Z_{\mu} e^{i\mathbf{G} \cdot \mathbf{d}_{\mu}} \right|^2 \frac{e^{-G^2/4\zeta}}{G^2}. \quad (49)$$

$E_{Ewald}^{(2)}$ is a rapidly convergent sum in real space, plus a term coming from the self-interaction of gaussians.

Miscellaneous

When a set of special points $\{\mathbf{k}_i\}$, with weights w_i , $\sum_i w_i = 1$, is used to sample the Brillouin Zone, one has:

$$\frac{1}{N} \sum_{\mathbf{k}} f(\mathbf{k}) \implies \sum_i w_i f(\mathbf{k}_i). \quad (50)$$

The $\psi(\mathbf{r})$ as defined above are vanishingly small in order to be normalized. What is actually calculated, and used in the Fast Fourier Transform algorithm, is $\sqrt{N}\psi(\mathbf{r})$: $\Psi(\mathbf{k} + \mathbf{G}) \xleftrightarrow{FFT} \sqrt{N}\psi(\mathbf{r})$. This ensures the correct normalization of the charge density.