

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 :

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

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

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

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

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

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

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

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 $\text{erf}(x) \rightarrow 2x/\sqrt{\pi}$ 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:

$$E_{Ewald}^{(2)} = \frac{1}{2} \int \tilde{n}(\mathbf{r}) \Phi(\mathbf{r}) d\mathbf{r} - e^2 \sqrt{\frac{\eta}{\pi}} \sum_{\mu} Z_{\mu}^2, \quad \tilde{n}(\mathbf{r}) = \sum_{\mu} Z_{\mu} \delta(\mathbf{r} - \mathbf{d}_{\mu}), \quad \Phi(\mathbf{r}) = e^2 \sum_{\mu, \mathbf{R}} \frac{Z_{\mu} \text{erf}(\sqrt{\eta} |\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{d}_{\mu} - \mathbf{R}|} \quad (25)$$

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

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

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

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

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

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

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

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

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:

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

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

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

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:

$$\frac{1}{N} \sum_{\mathbf{k}} f(\mathbf{k}) \implies \sum_i w_i f(\mathbf{k}_i). \tag{34}$$

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.

Matrix elements of non-local pseudopotentials

Semilocal form:

$$\hat{V}^\mu = V_\mu(r) + \sum_l V_{\mu,l}(r) \hat{P}_l \quad (35)$$

where $\hat{P}_l = |l\rangle\langle l|$ is the projector on angular momentum l . Using the expansion of plane waves into spherical harmonics Y_{lm} and spherical Bessel functions j_l :

$$e^{-i\mathbf{k}\cdot\mathbf{r}} = (2l+1) \sum_l i^l j_l(kr) P_l(\mathbf{k} \cdot \mathbf{r}) = 4\pi \sum_l i^l j_l(kr) \sum_m Y_{lm}^*(\mathbf{k}) Y_{lm}(\mathbf{r}) \quad (36)$$

one gets

$$V_{\mu,l}(\mathbf{k}_1, \mathbf{k}_2) = \frac{1}{\Omega} \int e^{-i\mathbf{k}_1 \cdot \mathbf{r}} V_{\mu,l}(\mathbf{r}) \hat{P}_l e^{i\mathbf{k}_2 \cdot \mathbf{r}} d\mathbf{r} = \frac{4\pi}{\Omega} (2l+1) P_l(\mathbf{k}_1 \cdot \mathbf{k}_2) \int_0^\infty r^2 j_l(k_1 r) j_l(k_2 r) V_{\mu,l}(r) dr = \frac{4\pi}{\Omega} (2l+1) P_l(\mathbf{k}_1 \cdot \mathbf{k}_2) F_l^\mu(k_1, k_2) \quad (37)$$

where the P_l are Lagrange polynomials. Using Bachelet-Hamann-Schlüter parameterization:

$$\hat{V}^\mu(\mathbf{r}) = -\frac{Z_\mu e^2}{r} \sum_{n=1}^{n_c} c_n^\mu \text{erf}(\sqrt{\alpha_n^\mu} r) + \sum_{l=0}^l \sum_{n=1}^{n_l} \left(A_{n,l}^\mu + A_{n+3,l}^\mu r^2 \right) e^{-\alpha_{n,l}^\mu r^2} \hat{P}_l \quad (38)$$

where $n_c = 2, n_l = 3$, the $F_l^\mu(k_1, k_2)$ have an analytical expression. For the α_μ one finds

$$\alpha_\mu = \int d\mathbf{r} \left(V_{loc}(r) + \frac{Z_\mu e^2}{r} \right) = 4\pi Z_\mu e^2 \int r^2 dr \left(\frac{-c_1 \text{erf}(\sqrt{\alpha_1} r) - (1-c_1) \text{erf}(\sqrt{\alpha_2} r)}{r} - \frac{1}{r} \right) = 4\pi Z_\mu e^2 \left(\frac{c_1}{4\alpha_1} + \frac{1-c_1}{4\alpha_2} \right). \quad (39)$$

Separable form:

$$\hat{V}^\mu = V_\mu(r) + \sum_l \frac{1}{v_l} f_{\mu,l}(r) f_{\mu,l}^*(r'). \quad (40)$$

For simplicity, we consider just one term per value of l . Using the same expansion as above one finds

$$V_{\mu,l}(\mathbf{k}_1, \mathbf{k}_2) = \frac{1}{\Omega} \frac{1}{v_l} \int e^{-i\mathbf{k}_1 \cdot \mathbf{r}} f_{\mu,l}(\mathbf{r}) d\mathbf{r} \int e^{i\mathbf{k}_2 \cdot \mathbf{r}'} f_{\mu,l}^*(\mathbf{r}') d\mathbf{r}' = \frac{4\pi}{\Omega} \frac{1}{v_l} \sum_{m=-l}^l \int r^2 j_l(k_1 r) f_{\mu,l}(\mathbf{r})(r) dr Y_{lm}(\hat{\mathbf{k}}_1) \int r^2 j_l(k_2 r) f_{\mu,l}^*(\mathbf{r})(r) dr Y_{lm}^*(\hat{\mathbf{k}}_2). \quad (41)$$

The angular term could be summed to yield Lagrange polynomials, but it is much more convenient to keep the “separated” form in Fourier space for computational purposes.

Beyond LDA

For spin-polarised systems, one introduces two distinct charge densities for spin up and down, n_σ , where $\sigma = +, -$, with $n(\mathbf{r})$ the total charge density, $n(\mathbf{r}) = n_+(\mathbf{r}) + n_-(\mathbf{r})$. The exchange-correlation energy E_{xc} is written as a functional of both n_σ 's:

$$E_{xc} = \int n(\mathbf{r}) \epsilon_{xc}(n_+(\mathbf{r}), n_-(\mathbf{r})) d\mathbf{r}. \quad (42)$$

The corresponding exchange-correlation potentials $V_{xc}^\sigma(\mathbf{r})$ are given by

$$V_{xc}^\sigma(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n_\sigma(\mathbf{r})} = \epsilon_{xc}(n_+(\mathbf{r}), n_-(\mathbf{r})) + n(\mathbf{r}) \frac{\delta \epsilon_{xc}(n_+(\mathbf{r}), n_-(\mathbf{r}))}{\delta n_\sigma(\mathbf{r})} = \epsilon_{xc}(n_+(\mathbf{r}), n_-(\mathbf{r})) + n(\mathbf{r}) \left. \frac{\partial \epsilon_{xc}(n_+, n_-)}{\partial n_\sigma} \right|_{n_+ = n_+(\mathbf{r}), n_- = n_-(\mathbf{r})} \quad (43)$$

(the functional derivatives can be performed as normal derivatives). Approximate forms of the exchange-correlation energy are traditionally expressed in terms of the density parameter $r_s = (3/4\pi n)^{1/3}$ and of the spin polarisation $\zeta = (n_+ - n_-)/n$. The following derivatives are useful in calculating the potential:

$$\frac{\partial r_s}{\partial n_\sigma} = -\frac{r_s}{3n} \quad , \quad \frac{\partial \zeta}{\partial n_\sigma} = -\frac{\zeta - \text{sgn}\sigma}{n} \quad (44)$$

where $\text{sgn}\sigma = +1$ if $\sigma = +$, $\text{sgn}\sigma = -1$ if $\sigma = -$. If $\epsilon_{xc} = \epsilon_{xc}(r_s, \zeta)$, the following expression holds for V_{xc}^σ :

$$V_{xc}^\sigma(r_s, \zeta) = \epsilon_{xc}(r_s, \zeta) - \frac{r_s}{3} \frac{\partial \epsilon_{xc}(r_s, \zeta)}{\partial r_s} - (\zeta - \text{sgn}\sigma) \frac{\partial \epsilon_{xc}(r_s, \zeta)}{\partial \zeta} \quad (45)$$

The exchange part, ϵ_x , of ϵ_{xc} is usually written as

$$\epsilon_x(r_s, \zeta) = -\frac{3}{4\pi r_s} \left(\frac{9\pi}{4} \right)^{1/3} \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}}{2}. \quad (46)$$

The corresponding exchange potential is given by

$$V_x^\sigma(r_s, \zeta) = \frac{4}{3} \epsilon_x(r_s, \zeta) + (\zeta - \text{sgn}\sigma) \frac{1}{\pi r_s} \left(\frac{9\pi}{4} \right)^{1/3} \frac{(1 + \zeta)^{1/3} - (1 - \zeta)^{1/3}}{2}. \quad (47)$$

Note that with the above form of ϵ_{xc} the exchange energy E_x is simply

$$E_x[n_+, n_-] = -\frac{3}{4} \left(\frac{6}{\pi} \right)^{1/3} \int [n_+(\mathbf{r})^{4/3} + n_-(\mathbf{r})^{4/3}] d\mathbf{r}. \quad (48)$$

Gradient-corrected functionals

The exchange-correlation energy E_{xc} is written as a functional of both n_σ 's and of the gradients ∇n_σ 's:

$$E_{xc} = \int n(\mathbf{r}) \epsilon_{xc}(n_+(\mathbf{r}), n_-(\mathbf{r}), \nabla n_+, \nabla n_-) d\mathbf{r}. \quad (49)$$

The corresponding exchange-correlation potentials $V_{xc}^\sigma(\mathbf{r})$ are given by

$$V_{xc}^\sigma(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n_\sigma(\mathbf{r})} = \frac{\partial F_{xc}}{\partial n_\sigma(\mathbf{r})} - \sum_\alpha \frac{\partial}{\partial \mathbf{r}_\alpha} \left[\frac{\partial F_{xc}}{\partial (\nabla_\alpha n_\sigma)} \right] = \frac{\partial F_{xc}}{\partial n_\sigma(\mathbf{r})} - \sum_\alpha \frac{\partial}{\partial \mathbf{r}_\alpha} \left[\frac{\partial F_{xc}}{\partial |\nabla n_\sigma|} \frac{\nabla_\alpha n_\sigma}{|\nabla n_\sigma|} \right] \quad (50)$$

where $F_{xc} = n\epsilon_{xc}$ and α denotes cartesian components. In plane-wave codes, the derivative in the second term is usually done using FFT.

Exchange: The gradient-corrected exchange energy E_x is usually written as

$$E_x[n_+, n_-, \nabla n_+, \nabla n_-] = \frac{1}{2} E_x[2n_+] + \frac{1}{2} E_x[2n_-] \quad (51)$$

where

$$E_x[n] = \int n \epsilon_x(r_s, s) d\mathbf{r} = \int n \epsilon_x^0(r_s) F(s) d\mathbf{r}, \quad \epsilon_x^0(r_s) = -\frac{3k_F}{4\pi} \quad (52)$$

where $k_F = (3\pi^2 n)^{1/3} = 1.9191583/r_s$, $s = |\nabla n|/2k_F n$, $\epsilon_x^0(r_s)$ is the usual Slater exchange and $F(s)$ is an “enhancement factor”
Each component (up and down) of the exchange potential contains a first term:

$$\frac{\partial}{\partial n_\sigma}(n \epsilon_x(r_s, s)) = \epsilon_x + n \frac{\partial \epsilon_x}{\partial n_\sigma} + n \frac{\partial \epsilon_x}{\partial s} \frac{\partial s}{\partial n_\sigma} = \frac{4}{3} \epsilon_x^0 F(s) + n \epsilon_x^0 \frac{dF}{ds} \frac{\partial s}{\partial n_\sigma} = \frac{4}{3} \epsilon_x^0 \left(F(s) - s \frac{dF}{ds} \right). \quad (53)$$

The last result uses the following identity:

$$\frac{\partial s}{\partial n_\sigma} = -\frac{|\nabla n|}{2n^2 k_F} \frac{\partial n}{\partial n_\sigma} - \frac{|\nabla n|}{2n k_F^2} \frac{\partial k_F}{\partial n_\sigma} = -\frac{|\nabla n|}{2n^2 k_F} - \frac{|\nabla n|}{2n k_F} \frac{1}{3n} = -\frac{4s}{3n}. \quad (54)$$

Second term of the exchange potential:

$$\frac{\partial}{\partial |\nabla n_\sigma|}(n \epsilon_x(r_s, s)) = n \frac{\partial \epsilon_x}{\partial s} \frac{\partial s}{\partial |\nabla n_\sigma|} = \frac{1}{2k_F} \frac{\partial \epsilon_x}{\partial s} = \frac{1}{2k_F} \epsilon_x^0 \frac{dF}{ds} = -\frac{3}{8\pi} \frac{dF}{ds} \quad (55)$$

Correlation: Gradient-correction contributions to the correlation energy E_c are usually expressed as a functions of variables t, r_s, ζ :

$$E_c[n_+, n_-, \nabla n_+, \nabla n_-] = \int n(\mathbf{r}) [\epsilon_c(r_s, \zeta) + H(t, r_s, \zeta)] d\mathbf{r}, \quad (56)$$

where $\epsilon_c(r_s, \zeta)$ is the LSDA correlation energy; $t = |\nabla n|/(2gnk_s)$, $g = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]/2$, $k_s = (4k_F/\pi)^{1/2}$. Note that $k_s^2/k_F^2 = 0.663436444r_s$.

Gradient-correction contribution to the correlation potential, first term:

$$\frac{\partial}{\partial n_\sigma}(nH(t, r_s, \zeta)) = H + n \frac{\partial H}{\partial n_\sigma} = H + n \frac{\partial H}{\partial t} \frac{\partial t}{\partial n_\sigma} + n \frac{\partial H}{\partial r_s} \frac{\partial r_s}{\partial n_\sigma} + n \frac{\partial H}{\partial \zeta} \frac{\partial \zeta}{\partial n_\sigma}. \quad (57)$$

Note that

$$\frac{\partial t}{\partial n_\sigma} = -\frac{|\nabla n|}{2g^2nk_s} \frac{\partial g}{\partial n_\sigma} - \frac{|\nabla n|}{2gn^2k_s} \frac{\partial n}{\partial n_\sigma} - \frac{|\nabla n|}{2gnk_s^2} \frac{\partial k_s}{\partial n_\sigma} = -\frac{|\nabla n|}{2gnk_s} \left(\frac{\partial g}{\partial \zeta} \frac{\partial \zeta}{\partial n_\sigma} + \frac{1}{n} + \frac{1}{6n} \right) = t \left(\frac{(1 + \zeta)^{-1/3} - (1 - \zeta)^{-1/3}}{3} \frac{\zeta - \text{sgn}\sigma}{n} + \frac{7}{6n} \right). \quad (58)$$

Using preceding results for $\partial r_s/\partial n_\sigma$ and $\partial \zeta/\partial n_\sigma$, one finds

$$\frac{\partial}{\partial n_\sigma}(nH(t, r_s, \zeta)) = H + t \left(\frac{(1 + \zeta)^{-1/3} - (1 - \zeta)^{-1/3}}{3} (\zeta - \text{sgn}\sigma) + \frac{7}{6} \right) \frac{\partial H}{\partial t} - \frac{r_s}{3} \frac{\partial H}{\partial r_s} - (\zeta - \text{sgn}\sigma) \frac{\partial H}{\partial \zeta}. \quad (59)$$

Second term for the correlation potential:

$$\frac{\partial}{\partial |\nabla n_\sigma|}(nH(t, r_s, \zeta)) = n \frac{\partial H}{\partial t} \frac{\partial t}{\partial |\nabla n_\sigma|} = \frac{1}{2gk_s} \frac{\partial H}{\partial t} \quad (60)$$

PW91 Gradient correction

Exchange term: the enhancement function F is given by

$$F(s) = \frac{1 + 0.19645s \sinh^{-1}(7.7956s) + (0.2743 - 0.1508e^{-100s^2})s^2}{1 + 0.19645s \sinh^{-1}(7.7956s) + 0.0004s^4}. \quad (61)$$

Correlation term: the function H is the sum of two terms, $H = H_0 + H_1$:

$$H_0 = g^3 \frac{\beta^2}{2\alpha} \log \left(1 + \frac{2\alpha}{\beta} t^2 \frac{1 + At^2}{1 + At^2 + A^2t^4} \right), \quad H_1 = \nu \left(C_c(r_s) - C_c(0) - \frac{3}{7} C_x \right) g^3 t^2 e^{-a_4(k_s^2/k_F^2)g^4t^2} \quad (62)$$

where

$$A = \frac{2\alpha}{\beta} \frac{1}{e^{-2\alpha\epsilon_c(r_s, \zeta)/(g^3\beta^2)} - 1}, \quad C_c(r_s) = -C_x + \frac{c_1 + c_2 r_s + c_3 r_s^2}{1 + c_4 r_s + c_5 r_s^2 + c_6 r_s^3}. \quad (63)$$

The numerical factors are: $\nu = (16/\pi)(3\pi^2)^{1/3} = 15.75592$, $C_c(0) = 0.004235$, $C_x = -0.001667212$, $\alpha = 0.09$, $c_1 = 0.002568$, $c_2 = 0.023266$, $c_3 = 7.389 \times 10^{-6}$, $c_4 = 8.723$, $c_5 = 0.472$, $c_6 = 7.389 \times 10^{-2}$, $a_4 = 100$, $\beta = \nu C_c(0)$.

Let us introduce the quantity B defined as:

$$B = \left(1 + \frac{2\alpha}{\beta} t^2 \frac{1 + At^2}{1 + At^2 + A^2 t^4}\right), \quad (64)$$

so that $H_0 = g^3(\beta^2/2\alpha)\log B$.

The derivatives with respect to r_s :

$$\frac{\partial H_0(r_s, t, \zeta)}{\partial r_s} = g^3 \frac{\beta^2}{2\alpha} \frac{1}{B} \frac{\partial B}{\partial A} \frac{\partial A}{\partial r_s}, \quad (65)$$

where

$$\frac{\partial B}{\partial A} = -\frac{2\alpha}{\beta} A t^6 \frac{2 + At^2}{(1 + At^2 + A^2 t^4)^2} \quad \frac{\partial A}{\partial r_s} = -\frac{4\alpha^2}{g^3 \beta^3} \frac{e^{-2\alpha\epsilon_c(r_s, \zeta)/(g^3\beta^2)}}{(e^{-2\alpha\epsilon_c(r_s, \zeta)/(g^3\beta^2)} - 1)^2} \frac{\partial \epsilon_c(r_s, \zeta)}{\partial r_s} \quad (66)$$

$$\frac{\partial H_1(r_s, t, \zeta)}{\partial r_s} = \nu \frac{dC_c(r_s)}{dr_s} g^3 t^2 e^{-a_4(k_s^2/k_F^2)g^4 t^2} - d_0 a_4 g^4 t^2 H_1 \quad (67)$$

where $d_0 = 0.663436444$ and

$$\frac{dC_c(r_s)}{dr_s} = \frac{(c_2 + 2c_3 r_s)(1 + c_4 r_s + c_5 r_s^2 + c_6 r_s^3) - (c_1 + c_2 r_s + c_3 r_s^2)(c_4 + 2c_5 r_s + 3c_6 r_s^2)}{(1 + c_4 r_s + c_5 r_s^2 + c_6 r_s^3)^2}. \quad (68)$$

The derivatives with respect to ζ :

$$\frac{\partial H_0(r_s, t, \zeta)}{\partial \zeta} = \frac{3}{g} H_0 \frac{\partial g}{\partial \zeta} + g^3 \frac{\beta^2}{2\alpha} \frac{1}{B} \frac{\partial B}{\partial A} \frac{\partial A}{\partial \zeta}. \quad (69)$$

where

$$\frac{\partial A}{\partial \zeta} = -\frac{4\alpha^2}{g^3 \beta^3} \frac{e^{-2\alpha\epsilon_c(r_s, \zeta)/(g^3\beta^2)}}{(e^{-2\alpha\epsilon_c(r_s, \zeta)/(g^3\beta^2)} - 1)^2} \left(\frac{\partial \epsilon_c(r_s, \zeta)}{\partial \zeta} - \frac{3\epsilon_c(r_s, \zeta)}{g} \frac{\partial g}{\partial \zeta} \right) \quad (70)$$

$$\frac{\partial H_1(r_s, t, \zeta)}{\partial r_s} = \left(\frac{3}{g} - 4a_4(k_s^2/k_F^2)g^3 t^2 \right) H_1 \frac{\partial g}{\partial \zeta}. \quad (71)$$

The derivatives with respect to t :

$$\frac{\partial H_0(r_s, t, \zeta)}{\partial \zeta} = g^3 \frac{\beta^2}{2\alpha} \frac{1}{B} \frac{\partial B}{\partial t} \quad (72)$$

where

$$\frac{\partial B}{\partial t} = \frac{4\alpha}{\beta} t \frac{1 + At^2}{1 + At^2 + A^2 t^4} + \frac{2\alpha}{\beta} t^2 \frac{(1 + 2At)(1 + At^2 + A^2 t^4) - (1 + At^2)(2At + 4A^2 t^3)}{(1 + At^2 + A^2 t^4)^2} \quad (73)$$

$$\frac{\partial H_1(r_s, t, \zeta)}{\partial r_s} = \left(\frac{2}{t} - 2a_4(k_s^2/k_F^2)g^4 t \right) H_1. \quad (74)$$