Computer lab: density functional perturbation theory for lattice dynamics

Andrea Dal Corso

SISSA and DEMOCRITOS
Trieste (Italy)

Outline

1. The dynamical matrix
2. The bare perturbation
3. The induced charge density
4. The linear system
5. The induced potential

Dynamical matrix

We want to write a small computer program that calculates the dynamical matrix of a solid:

$$
\begin{aligned}
D_{s\alpha s'\beta}(\mathbf{q}) &= \int_\Omega d^3r \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mathbf{u}^*_{s\alpha}(\mathbf{q}) \partial \mathbf{u}_{s'\beta}(\mathbf{q})} \rho(\mathbf{r}) \leftarrow I_1 \\
&+ \int_\Omega d^3r \left(\frac{\partial \tilde{V}_{\mathrm{loc}}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})} \right)^* \left(\frac{\tilde{\partial}\rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} \right) \leftarrow I_2 \\
&+ D^{Ewald}_{s\alpha s'\beta}(\mathbf{q}) \leftarrow I_3.
\end{aligned}
$$

We need three routines: `dynmat0`, `drhodv` and `d2ionq` to calculate I_1, I_2 and I_3 respectively.

dynmat0

I_1 can be calculated using the charge density only. It is calculated in reciprocal space. Writing:

$$\begin{aligned} V_{\mathrm{loc}}(\mathbf{r}) &= \sum_{\mu,s} v^s_{\mathrm{loc}}(\mathbf{r} - \mathbf{R}_\mu - \mathbf{d}_s - \mathbf{u}_{\mu,s}) \\ &= \sum_{\mu,s}\sum_{\mathbf{k}} v^s_{\mathrm{loc}}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{R}_\mu} e^{-i\mathbf{k}\cdot\mathbf{d}_s} e^{-i\mathbf{k}\cdot\mathbf{u}_{\mu,s}}, \end{aligned}$$

where $v^s_{\mathrm{loc}}(\mathbf{k}) = \frac{1}{V}\int d^3r\ v^s_{\mathrm{loc}}(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}$ is the Fourier transform of $v^s_{\mathrm{loc}}(\mathbf{r})$, we have that:

$$\frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mathbf{u}^*_{s\alpha}(\mathbf{q}) \partial \mathbf{u}_{s'\beta}(\mathbf{q})} = -\delta_{s,s'} \sum_G \tilde{v}^s_{\mathrm{loc}}(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{d}_s} \mathbf{G}_\alpha \mathbf{G}_\beta e^{i\mathbf{G}\cdot\mathbf{r}},$$

where $\tilde{v}^s_{\mathrm{loc}}(\mathbf{G}) = \frac{1}{\Omega}\int d^3r\ v^s_{\mathrm{loc}}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}$.

dynmat0 - I

Writing the charge density in Fourier series:

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}},$$

I_1 is:

$$I_1 = -\delta_{s,s'}\Omega \sum_{\mathbf{G}} \rho(\mathbf{G}) \tilde{v}^s_{\mathrm{loc}}(\mathbf{G})^* e^{i\mathbf{G}\cdot\mathbf{d}_s} \mathbf{G}_\alpha \mathbf{G}_\beta.$$

`dynmat0` calculates this sum using the fact that $\tilde{v}^s_{\mathrm{loc}}(\mathbf{G})$ is real and this integral is also real. So

$$I_1 = -\delta_{s,s'}\Omega \sum_{\mathbf{G}} \tilde{v}^s_{\mathrm{loc}}(\mathbf{G}) \mathbf{G}_\alpha \mathbf{G}_\beta \left[\Re\rho(\mathbf{G}) cos(\mathbf{G}\cdot\mathbf{d}_s) - \Im\rho(\mathbf{G}) sin(\mathbf{G}\cdot\mathbf{d}_s) \right].$$

dynmat0 - II

Note that we will calculate the phonon frequencies of Si using the Appelbaum and Hamann pseudo-potential so:

$$\Omega \tilde{v}^{s}_{\mathrm{loc}}(\mathbf{k}) = e^{-\frac{\mathbf{k}^2}{4\alpha}} \left\{ -\frac{4\pi Z_v e^2}{|\mathbf{k}|^2} + \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}} \left[v_1 + \frac{v_2}{\alpha}\left(\frac{3}{2} - \frac{|\mathbf{k}|^2}{4\alpha}\right)\right]\right\}$$

where

$$\begin{aligned} Z_v &= 4 \\ v_1 &= 3.042\ Ha \\ v_2 &= -1.372\ Ha \\ \alpha &= 0.6102\ 1/(a.u.)^2 \end{aligned}$$

The bare perturbation

To calculate I_2 we need the periodic part of the bare perturbation $\frac{\partial \tilde{V}_{\mathrm{loc}}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})}$. We have:

$$\begin{aligned}\frac{\partial V_{\mathrm{loc}}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})} &= \sum_{\mu} e^{i\mathbf{q}\cdot\mathbf{R}_\mu} \frac{\partial V_{\mathrm{loc}}(\mathbf{r})}{\partial \mathbf{u}_{\mu s\alpha}} \\ &= -i \sum_{G} \tilde{v}^{s}_{\mathrm{loc}}(\mathbf{q}+\mathbf{G})(\mathbf{q}+\mathbf{G})_\alpha e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{d}_s} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}.\end{aligned}$$

Therefore the periodic part has Fourier components:

$$\frac{\partial \tilde{V}_{\mathrm{loc}}(\mathbf{q}+\mathbf{G})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})} = -i\tilde{v}^{s}_{\mathrm{loc}}(\mathbf{q}+\mathbf{G})(\mathbf{q}+\mathbf{G})_\alpha e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{d}_s}.$$

This expression is calculated by the routine `compute_dvloc`.

Charge density response

Then we need the lattice-periodic part of the induced charge density which is:

$$\frac{\partial\tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = 2\sum_{\mathbf{k}v} u^*_{\mathbf{k}v}(\mathbf{r}) P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial\tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}.$$

The routine `incdrhoscf` calculates this expression after the calculation of $P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial\tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$. Note that if each band is occupied by 2 electrons, in the nonmagnetic case, we need another factor of 2 for spin degeneracy. The sum over $\mathbf{k}$ is done as in the calculation of the charge density.

The linear system

$P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$ is the solution of the linear system:

$$\left[H^{\mathbf{k}+\mathbf{q}} + Q - \epsilon_{\mathbf{k}v}\right] P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = -P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{V}_{KS}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} u_{\mathbf{k}v}(\mathbf{r}).$$

This linear system is solved by an iterative conjugate gradient algorithm that requires a routine that applies the left hand side to an arbitrary function and a routine that computes the right hand side. The left hand side is applied by the routine `ch_psi_all`, while the right hand side is calculated from the induced Kohn and Sham potential.

ch_psi_all - II

The operator $Q = \sum_v \alpha |u_{\mathbf{k}+\mathbf{q}v}\rangle\langle u_{\mathbf{k}+\mathbf{q}v}|$ vanishes when applied to $P_c^{\mathbf{k}+\mathbf{q}}$ so it will not change the solution. If $\alpha > \max(\epsilon_{\mathbf{k}v} - \epsilon_{\mathbf{k}+\mathbf{q}v'})$ it makes the operator $H^{\mathbf{k}+\mathbf{q}} + Q - \epsilon_{\mathbf{k}v}$ nonsingular and the linear system well defined. We take $\alpha = 2(\max(\epsilon_{\mathbf{k}v}) - \min(\epsilon_{\mathbf{k}v}))$ and the same α is used for all $\mathbf{k}$ points.

The induced potential

The induced potential is given by:

$$\frac{\partial \tilde{V}_{KS}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \frac{\partial \tilde{V}_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} + \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} e^{i\mathbf{q}(\mathbf{r}'-\mathbf{r})} \frac{\partial \tilde{\rho}(\mathbf{r}')}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} + \frac{\partial V_{xc}(\mathbf{r})}{\partial \rho} \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}.$$

The first term is calculated by `compute_dvloc`, while the other two terms are calculated by `dv_of_drho`.

dv_of_drho

The induced exchange and correlation potential is calculated in real space. $\frac{\partial V_{xc}(\mathbf{r})}{\partial \rho}$ is calculated at the beginning of the run by `phq_init` and `dmxc` by numerical differentiation:

$$\frac{\partial V_{xc}(\mathbf{r})}{\partial \rho} = \Big[V_{xc}(\mathbf{r}, \rho + \Delta) - V_{xc}(\mathbf{r}, \rho - \Delta) \Big] / 2\Delta,$$

and the induced exchange and correlation potential is calculated in real space:

$$\frac{\partial V_{xc}(\mathbf{r})}{\partial \rho} \frac{\tilde{\partial} \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}.$$

dv_of_drho - II

The induced Hartree potential is calculated in reciprocal space, and a Fourier transform is later used to calculate it in real space. We have:

$$\begin{aligned}
& \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} e^{i\mathbf{q}(\mathbf{r}'-\mathbf{r})} \frac{\partial\tilde{\rho}(\mathbf{r}')}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} \\
= \quad & e^{-i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} \frac{\partial\tilde{\rho}(\mathbf{q}+\mathbf{G})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'} \\
= \quad & \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \frac{\partial\tilde{\rho}(\mathbf{q}+\mathbf{G})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} 4\pi \frac{1}{|\mathbf{q}+\mathbf{G}|^2},
\end{aligned}$$

where $\frac{\partial\tilde{\rho}(\mathbf{q}+\mathbf{G})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$ is calculated by a Fourier transform of $\frac{\partial\tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$.

Putting all together: solve_linter

We need a driver to solve the self-consistent linear system. The driver is `solve_linter`. This routine allocates space for the input and output induced potential, apply $\frac{\partial \tilde{V}_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$ (using `dvqpsi`) and the input induced potential to $u_{\mathbf{k}V}(\mathbf{r})$, and apply the projector $P_c^{\mathbf{k}+\mathbf{q}}$ to prepare the right hand side of the linear system. Then it calls `cgsolve_all` to solve the linear system and `incdrhoscf` to calculate the contribution of the **k** point to the induced charge density. These steps are repeated for all **k** points and then `dv_of_drho` is used to calculate the output induced potential. Finally a mixing routine checks if self-consistency has been achieved. If not the mixing routine provides the input induced potential for the next iteration.

drhodv

After the self-consistent solution of the linear system we obtain the self-consistent induced charge density $\frac{\partial\tilde{\rho}(\mathbf{r})}{\partial\mathbf{u}_{s'\beta}(\mathbf{q})}$. After a Fourier transform of $\frac{\partial\tilde{V}_{\mathrm{loc}}(\mathbf{q}+\mathbf{G})}{\partial\mathbf{u}_{s\alpha}(\mathbf{q})}$ we get $\frac{\partial\tilde{V}_{\mathrm{loc}}(\mathbf{r})}{\partial\mathbf{u}_{s\alpha}(\mathbf{q})}$ and

$$I_2 = \frac{\Omega}{N_1 \times N_2 \times N_3} \sum_i \left(\frac{\partial\tilde{V}_{\mathrm{loc}}(\mathbf{r}_i)}{\partial\mathbf{u}_{s\alpha}(\mathbf{q})}\right)^* \left(\frac{\partial\tilde{\rho}(\mathbf{r}_i)}{\partial\mathbf{u}_{s'\beta}(\mathbf{q})}\right),$$

where the sum is over all the points of the real space mesh and N_1, N_2 and N_3 are the dimensions of the mesh.

d2ionq

$$
\begin{aligned}
{}^{ion}\tilde{C}^{\alpha\beta}_{st}(\mathbf{q}) = & \frac{4\pi e^2}{\Omega}\sum_{\mathbf{G}} \frac{e^{-(\mathbf{q}+\mathbf{G})^2/4\eta}}{(\mathbf{q}+\mathbf{G})^2} Z_s Z_t \\
& \times e^{i(\mathbf{q}+\mathbf{G})\cdot(\tau_s-\tau_t)}(q_\alpha+G_\alpha)(q_\beta+G_\beta) \\
& - \frac{2\pi e^2}{\Omega}\sum_{\mathbf{G}\neq 0} \frac{e^{-G^2/4\eta}}{G^2} \\
& \times \left[Z_s \sum_l Z_l e^{i\mathbf{G}\cdot(\tau_s-\tau_l)} G_\alpha G_\beta + \text{c.c.} \right] \delta_{st} \\
& + e^2 \sum_{\mathbf{R}} Z_s Z_t e^{i\mathbf{q}\cdot\mathbf{R}} \\
& \times [\delta_{\alpha\beta} f_2(x) + f_1(x) x_\alpha x_\beta]_{\mathbf{x}=\tau_s-\tau_t-\mathbf{R}} \\
& - e^2 \delta_{st} \sum_{\mathbf{R}} \sum_l Z_s Z_l \\
& \times [\delta_{\alpha\beta} f_2(x) + f_1(x) x_\alpha x_\beta]_{\mathbf{x}=\tau_s-\tau_l-\mathbf{R}} \qquad \text{(B2)}
\end{aligned}
$$

where the sum over $\mathbf{G}$ space excludes $\mathbf{q}+\mathbf{G}=0$, the sums over $\mathbf{R}$ space exclude $\tau_s-\tau_t-\mathbf{R}=0$, and the functions f_1 and f_2 are defined as

$$
f_1(r) = \frac{3\,\text{erfc}(\sqrt{\eta}r) + 2\sqrt{\frac{\eta}{\pi}} r (3+2\eta r^2) e^{-\eta r^2}}{r^5}, \qquad \text{(B3)}
$$

$$
f_2(r) = \frac{-\text{erfc}(\sqrt{\eta}r) - 2\sqrt{\frac{\eta}{\pi}} r e^{-\eta r^2}}{r^3}. \qquad \text{(B4)}
$$

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dyndia

Finally we need a driver for the diagonalization of the dynamical matrix. The driver is `dyndia`. It divides the dynamical matrix by the masses, it forces it to be exactly Hermitian, it calls the routine `cdiagh` to diagonalize it and writes on output the frequencies. Imaginary frequencies are written with a minus sign.

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