Computer lab: density functional perturbation theory for lattice dynamics

Andrea Dal Corso

SISSA and DEMOCRITOS
Trieste (Italy)

Outline

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 $\alpha > \max(\epsilon_{\mathbf{k}v} - \epsilon_{\mathbf{k}v'})$ 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

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

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

Rev. Mod. Phys. **73**, 515 (2001).

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.

Bibliography

1 S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987); P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).

2 S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).

3 A. Dal Corso, Phys. Rev. B **64**, 235118 (2001).

4 A. Dal Corso, Phys. Rev. B **76**, 054308 (2007).

5 A. Dal Corso, Phys. Rev. B **81**, 075123 (2010).