Density functional perturbation theory for lattice dynamics with ultrasoft pseudopotentials and PAW

Andrea Dal Corso

SISSA and DEMOCRITOS
Trieste (Italy)

Outline

US-PPs Hamiltonian

$$\left[-\frac{1}{2}\nabla^2 + V_{NL} + \int d^3r\ V^{\sigma}_{eff}(\mathbf{r})K(\mathbf{r})\right]|\psi_{i\sigma}\rangle = \varepsilon_{i\sigma}S|\psi_{i\sigma}\rangle,$$

$$V^{\sigma}_{eff}(\mathbf{r}) = V_{loc}(\mathbf{r}) + \int d^3r_1\ \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|} + V^{\sigma}_{xc}(\mathbf{r}),$$

$$V_{NL}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{Inm} D^{(0)\gamma(I)}_{nm}\beta^{\gamma(I)}_n(\mathbf{r}_1-\mathbf{R}_I)\beta^{*\gamma(I)}_m(\mathbf{r}_2-\mathbf{R}_I),$$

$$\rho_\sigma(\mathbf{r}) = \sum_i \tilde{\theta}_{F,i\sigma}\langle\psi_{i\sigma}|K(\mathbf{r})|\psi_{i\sigma}\rangle,$$

$$\begin{aligned} K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2) &= \delta(\mathbf{r}-\mathbf{r}_1)\delta(\mathbf{r}-\mathbf{r}_2) \\ &+ \sum_{Inm} Q^{\gamma(I)}_{nm}(\mathbf{r}-\mathbf{R}_I)\beta^{\gamma(I)}_n(\mathbf{r}_1-\mathbf{R}_I)\beta^{*\gamma(I)}_m(\mathbf{r}_2-\mathbf{R}_I). \end{aligned}$$

US-PPs - Perturbation

Atoms move:

$$\mathbf{R}_I = \mathbf{R}_\ell + \mathbf{d}_s \rightarrow \mathbf{R}_\ell + \mathbf{d}_s + \mathbf{u}(\ell, s)$$

V_{loc}, V_{NL}, K, the overlap matrix

$$S(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2) + \sum_{Inm} q_{nm}^{\gamma(I)} \beta_n^{\gamma(I)}(\mathbf{r}_1 - \mathbf{R}_I) \beta_m^{*\gamma(I)}(\mathbf{r}_2 - \mathbf{R}_I),$$

and the ortogonality constraint:

$$\langle \psi_{i\sigma} | S | \psi_{j\sigma} \rangle = \delta_{ij},$$

depend on the perturbation. Calling λ the perturbation, we have

$$\langle \frac{d\psi_{i\sigma}}{d\lambda} | S | \psi_{j\sigma} \rangle + \langle \psi_{i\sigma} | S | \frac{d\psi_{j\sigma}}{d\lambda} \rangle = -\langle \psi_{i\sigma} | \frac{\partial S}{\partial \lambda} | \psi_{j\sigma} \rangle,$$

US-PPs - Induced charge

$$\frac{d\rho_\sigma(\mathbf{r})}{d\mu} = 2\,\mathrm{Re}\sum_i \langle\psi_{i\sigma}|K(\mathbf{r})|\Delta^\mu\psi_{i\sigma}\rangle - \sum_i \langle\psi_{i\sigma}|K(\mathbf{r})|\delta^\mu\psi_{i\sigma}\rangle$$

$$+ \sum_i \tilde{\theta}_{F,i\sigma}\langle\psi_{i\sigma}|\frac{\partial K(\mathbf{r})}{\partial\mu}|\psi_{i\sigma}\rangle.$$

We call $\Delta^\mu\rho_\sigma(\mathbf{r})$ the last two terms.

$$|\delta^\mu\psi_{i\sigma}\rangle = \sum_j \left[\tilde{\theta}_{F,i\sigma}\theta_{i\sigma,j\sigma} + \tilde{\theta}_{F,j\sigma}\theta_{j\sigma,i\sigma}\right]|\psi_{j\sigma}\rangle\langle\psi_{j\sigma}|\frac{\partial S}{\partial\mu}|\psi_{i\sigma}\rangle.$$

$|\tilde{\Delta}^\mu\psi_{i\sigma}\rangle = |\Delta^\mu\psi_{i\sigma}\rangle - \frac{1}{2\eta}\tilde{\delta}_{F,i\sigma}\frac{d\varepsilon_F}{d\mu}|\psi_{i\sigma}\rangle$ is the solution of:

US-PPs - Linear system

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}^{\sigma} + Q^{\sigma} - \varepsilon_{i\sigma} S\right] |\tilde{\Delta}^{\mu}\psi_{i\sigma}\rangle = -P_{c,i\sigma}^{\dagger}\left[\frac{dV_{KS}^{\sigma}}{d\mu} - \varepsilon_{i\sigma}\frac{\partial S}{\partial \mu}\right] |\psi_{i\sigma}\rangle,$$

with

$$P_{c,i\sigma}^{\dagger} = \left[\tilde{\theta}_{F,i\sigma} - \sum_{j} \beta_{i\sigma,j\sigma} S |\psi_{j\sigma}\rangle\langle\psi_{j\sigma}|\right].$$

and

$$V_{KS}^{\sigma}(\mathbf{r}_1, \mathbf{r}_2) = V_{NL}(\mathbf{r}_1, \mathbf{r}_2) + \int d^3r \; V_{eff}^{\sigma}(\mathbf{r}) K(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2).$$

US-PPs - First derivatives of the KS potential

$$\frac{dV^{\sigma}_{KS}(\mathbf{r}_1,\mathbf{r}_2)}{d\mu} = \frac{\partial V^{\sigma}_{KS}(\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu} + \int d^3r\, \frac{dV^{\sigma}_{Hxc}(\mathbf{r})}{d\mu} K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2).$$

$$\frac{\partial V^{\sigma}_{KS}(\mathbf{r}_1,\mathbf{r}_2)}{\partial\lambda} = \frac{\partial V_{NL}(\mathbf{r}_1,\mathbf{r}_2)}{\partial\lambda} + \int d^3r\, \frac{\partial V_{loc}(\mathbf{r})}{\partial\lambda} K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2) + \int d^3r\, V^{\sigma}_{eff}(\mathbf{r}) \frac{\partial K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2)}{\partial\lambda}.$$

US-PPs - Second derivatives of the energy

$$\frac{d^2 F^{(1)}_{tot}}{d\mu d\lambda} = \sum_{i\sigma} \tilde{\theta}_{F,i\sigma} \langle \psi_{i\sigma} | \left[\frac{\partial^2 V^{\sigma}_{KS}}{\partial\mu\partial\lambda} - \varepsilon_{i\sigma} \frac{\partial^2 S}{\partial\mu\partial\lambda} \right] | \psi_{i\sigma} \rangle,$$

$$\frac{d^2 F^{(2)}_{tot}}{d\mu d\lambda} = 2 \,\mathrm{Re} \sum_{i\sigma} \langle \Delta^{\mu} \psi_{i\sigma} | \left[\frac{\partial V^{\sigma}_{KS}}{\partial\lambda} - \varepsilon_{i\sigma} \frac{\partial S}{\partial\lambda} \right] | \psi_{i\sigma} \rangle,$$

$$\frac{d^2 F^{(3)}_{tot}}{d\mu d\lambda} = \sum_{\sigma} \int d^3 r \, \frac{dV^{\sigma}_{Hxc}(\mathbf{r})}{d\mu} \Delta^{\lambda} \rho_{\sigma}(\mathbf{r}),$$

$$\frac{d^2 F^{(4)}_{tot}}{d\mu d\lambda} = - \sum_{i\sigma} \left\{ \langle \delta^{\mu} \psi_{i\sigma} | \left[\frac{\partial V^{\sigma}_{KS}}{\partial\lambda} - \varepsilon_{i\sigma} \frac{\partial S}{\partial\lambda} \right] | \psi_{i\sigma} \rangle + (\mu \leftrightarrow \lambda) \right\}.$$

US-PPs - Second partial derivatives of the KS potential

$$
\begin{aligned}
\frac{\partial^2 V^{\sigma}_{KS}(\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu\partial\lambda} &= \frac{\partial^2 V_{NL}(\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu\partial\lambda} \\
&+ \int d^3r\, \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial\mu\partial\lambda} K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2) \\
&+ \int d^3r\, V^{\sigma}_{eff}(\mathbf{r}) \frac{\partial^2 K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu\partial\lambda} \\
&+ \left[\int d^3r\, \frac{\partial V_{loc}(\mathbf{r})}{\partial\lambda} \frac{\partial K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu} + (\lambda \leftrightarrow \mu)\right].
\end{aligned}
$$

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

The dynamical matrix

The dynamical matrix is:

$$\Phi_{\alpha\beta}\left(\mathbf{q}, s, s'\right) = \frac{1}{N} \sum_{\ell\ell'} e^{-i\mathbf{q}\cdot\mathbf{R}_\ell} \frac{d^2 F_{tot}}{d\mathbf{u}_\alpha(\ell, s) d\mathbf{u}_\beta(\ell', s')} e^{i\mathbf{q}\cdot\mathbf{R}_{\ell'}},$$

So we take $\mu \to \mathbf{u}_\alpha(\ell, s)$ and $\lambda \to \mathbf{u}_\beta(\ell', s')$.
In a periodic solid the index i on the wavefunctions becomes a Bloch vector and a band index $\mathbf{k}$, v.

US - PPs Changes summary

- Compute $\Delta^\mu \rho_\sigma(\mathbf{r})$. drho.f90, incdrhous.f90, compute_drhous.f90.
- Compute $\frac{d^2 F^{(4)}_{tot}}{d\mu d\lambda}$. drho.f90, compute_nldyn.f90.
- Add the contributions to $\frac{\partial^2 V^\sigma_{KS}(\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu\partial\lambda}$. dvanqq.f90, dynmat_us.f90, addusdynmat.f90.
- Add the contributions to $\frac{\partial V^\sigma_{KS}(\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu}$. dvqpsi_us_only.f90.
- Add the contributions to $\frac{dV^\sigma_{KS}(\mathbf{r}_1,\mathbf{r}_2)}{d\mu}$. newdq.f90, adddvscf.f90.
- Add the augmentation charge to the induced charge. addusddens.f90.
- Compute $\frac{d^2 F^{(3)}_{tot}}{d\mu d\lambda}$. drhodvus.f90.
- Add the contributions to $\frac{d^2 F^{(2)}_{tot}}{d\mu d\lambda}$. drhodvnl.f90.

PAW - Hamiltonian

$$\left[-\frac{1}{2}\nabla^2 + V_{NL} + \int d^3r \; V^{\sigma}_{eff}(\mathbf{r})K(\mathbf{r})\right]|\psi_{i\sigma}\rangle = \varepsilon_{i\sigma} S|\psi_{i\sigma}\rangle,$$

$$V_{NL}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{Inm} \left(D^{1,\sigma}_{I,nm} - \tilde{D}^{1,\sigma}_{I,nm}\right)\beta^{\gamma(I)}_n(\mathbf{r}_1 - \mathbf{R}_I)\beta^{*\gamma(I)}_m(\mathbf{r}_2 - \mathbf{R}_I),$$

$$\rho_\sigma(\mathbf{r}) = \sum_i \tilde{\theta}_{F,i\sigma}\langle\psi_{i\sigma}|K(\mathbf{r})|\psi_{i\sigma}\rangle,$$

$$\begin{aligned} K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2) &= \delta(\mathbf{r}-\mathbf{r}_1)\delta(\mathbf{r}-\mathbf{r}_2) \\ &+ \sum_{Inm} Q^{\gamma(I)}_{nm}(\mathbf{r}-\mathbf{R}_I)\beta^{\gamma(I)}_n(\mathbf{r}_1 - \mathbf{R}_I)\beta^{*\gamma(I)}_m(\mathbf{r}_2 - \mathbf{R}_I). \end{aligned}$$

L. Paulatto, G. Fratesi, and S. de Gironcoli, unpublished.

PAW - Hamiltonian

$$D^{1,\sigma}_{I,mn} = \int_{\Omega_I} d^3r\, \Phi^{I,AE}_m(\mathbf{r})(-\frac{1}{2}\nabla^2)\Phi^{I,AE}_n(\mathbf{r}) + \int_{\Omega_I} d^3r\, \Phi^{I,AE}_m(\mathbf{r})\Phi^{I,AE}_n(\mathbf{r})\, V^{I,\sigma}_{eff}(\mathbf{r}),$$

$$\tilde{D}^{1,\sigma}_{I,mn} = \int_{\Omega_I} d^3r\, \Phi^{I,PS}_m(\mathbf{r})(-\frac{1}{2}\nabla^2)\Phi^{I,PS}_n(\mathbf{r}) + \int_{\Omega_I} d^3r\, \Phi^{I,PS}_m(\mathbf{r})\Phi^{I,PS}_n(\mathbf{r})\, \tilde{V}^{I,\sigma}_{eff}(\mathbf{r}) + \int_{\Omega_I} d^3r\, Q_{I,mn}(\mathbf{r})\, \tilde{V}^{I,\sigma}_{eff}(\mathbf{r})$$

$D^{1,\sigma}_{I,mn}$ and $\tilde{D}^{1,\sigma}_{I,mn}$ depend on the atomic positions through $V^{I,\sigma}_{eff}(\mathbf{r})$ and $\tilde{V}^{I,\sigma}_{eff}(\mathbf{r})$, respectively.

PAW - Induced charge

In real space as US-PPs, while within the spheres:

$$\frac{d\rho_{\sigma}^{1,I}(\mathbf{r})}{d\mu} = \sum_{mn} \langle \Phi_m^{I,AE} | \mathbf{r} \rangle \langle \mathbf{r} | \Phi_n^{I,AE} \rangle \frac{d\rho_{mn}^{I,\sigma}}{d\mu},$$

$$\rho_{mn}^{I,\sigma} = \sum_i \tilde{\theta}_{F,i\sigma} \langle \psi_{i,\sigma} | \beta_m^I \rangle \langle \beta_n^I | \psi_{i,\sigma} \rangle$$

$$\frac{d\rho_{mn}^{I,\sigma}}{d\mu} = 2Re \sum_i \langle \psi_{i,\sigma} | \beta_m^I \rangle \langle \beta_n^I | \Delta^{\mu} \psi_{i,\sigma} \rangle + b_{I,mn}^{\sigma,\mu}.$$

$$b_{I,mn}^{\sigma,\mu} = \sum_i \tilde{\theta}_{F,i\sigma} \langle \psi_{i,\sigma} | \frac{\partial \left(|\beta_m^I\rangle \langle \beta_n^I| \right)}{\partial \mu} | \psi_{i,\sigma} \rangle - \sum_i \langle \psi_{i,\sigma} | \beta_m^I \rangle \langle \beta_n^I | \delta^{\mu} \psi_{i,\sigma} \rangle,$$

PAW - Linear system

$$[H^\sigma + Q^\sigma - \varepsilon_{i\sigma} S] \, |\tilde{\Delta}^\mu \psi_{i\sigma}\rangle = -P^\dagger_{c,i\sigma} \left[\frac{dH^\sigma}{d\mu} - \varepsilon_{i\sigma} \frac{\partial S}{\partial \mu} \right] |\psi_{i\sigma}\rangle,$$

$$\frac{dH^\sigma}{d\mu} = \frac{dV^\sigma_{KS}}{d\mu} + \sum_{I,mn} \Delta D^{1,\sigma,\mu}_{I,mn} |\beta^I_m\rangle\langle\beta^I_n|,$$

where $\Delta D^{1,\sigma,\mu}_{I,mn} = \left(\frac{dD^{1,\sigma}_{I,mn}}{d\mu} - \frac{d\tilde{D}^{1,\sigma}_{I,mn}}{d\mu} \right)$.

$$\frac{dD^{1,\sigma}_{I,mn}}{d\mu} = \sum_{\sigma_1} \int_{\Omega_I} d^3r \; \Phi^{I,AE}_m(\mathbf{r}) \Phi^{I,AE}_n(\mathbf{r}) \frac{dV^{I,\sigma}_{eff}}{d\rho^{1,I}_{\sigma_1}} \frac{d\rho^{1,I}_{\sigma_1}}{d\mu}.$$

PAW - Second derivatives of the energy

Terms (1), (2), (4) as with US-PPs, only the term (3) has a PAW contribution:

$$\frac{d^2 E_{tot}^{(3)}}{d\mu d\lambda} = \frac{d^2 E_{tot}^{(3)US}}{d\mu d\lambda} + \sum_{\sigma} \sum_{I,mn} \Delta D_{I,mn}^{1,\sigma,\mu} b_{I,mn}^{\sigma,\lambda}.$$

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

PAW - Changes summary

- Save $b^{\sigma,\lambda}_{I,mn}$ when computed. drho.f90, addusddens.f90.
- Compute $\Delta D^{1,\sigma,\mu}_{I,mn}$ inside the spheres. PAW_dpotential, PAW_dusymmetrize.
- Add the contributions to $\frac{dH^{\sigma}}{d\mu}$ newdq.f90.
- Add the PAW contribution to $\frac{d^2 F^{(3)}_{tot}}{d\mu d\lambda}$. drhodvus.f90.

Phonon parallelization: grid, images

Parallelization modes of QE:

- **G**-vectors.
- bands.
- **k**-points.

Additional parallelization of phonon:

- **q**-vectors.
- Irreducible representations.

Actually this is implemented using `grid` techniques: one **q** point per run or one `irrep` per run.
Another possibility is to use `images`. The total number of processors is split into several groups (images) each image running an independent copy of `ph.x`.

Phonon parallelization: grid, images

Problems with the grid:

- It requires complex scripts to coordinate and collect the results of different runs.

Problems with images:

- Images do not communicate among themselves, because different runs are independent.
- Load balacing is difficult.
- Final results need to be collected running `ph.x` another time.

The future: thermo_pw

`thermo_pw` solves two of these problems:

- Images can communicate through a master-slaves approach via MPI calls.
- The code can run in a synchronous and asynchronous mode. It can collect the final results automatically.
- The code can mix calls to `pw.x` and `ph.x` so that it is possible for instance to optimize the structure before calling `ph.x`, or call `ph.x` for several geometries and compute anharmonic properties.

Asynchronous parallelization via MPI routines

Both master and slaves compute all the tasks to do (for instance all the `irreps` and **q** points) and assign a number to each task.

Master:

1. During initialization calls a nonblocking receive of the `ready` variable from all the slaves (`mpi_irecv`).
2. Tests if some slave has sent the `ready` variable (`mpi_test`).
3. If not, it continues its work. If a slave has sent its `ready` variable it sends (with a blocking send) to the slave the number of the next task to do (`mpi_send`) or the `no_work` number if there is no more work to do.
4. Finally makes another nonblocking receive of the `ready` variable from the slave that has received the work to do and continues its work.

Asynchronous parallelization via MPI routines

Slave:

1. Sends (with a blocking send) the `ready` variable to the master (`mpi_send`).
2. Receives (with a blocking receive) the number of the task to do. When it receives it, it starts to do its work or exit if the task number corresponds to `no_work` (`mpi_receive`).
3. When it finishes its task it restarts from [1]

To coordinate the work it is sufficient to initialize the master doing [1] at the beginning of the asynchronous work and that the master calls as often as possible a routine that executes [2], [3], [4] (for instance after each scf step). The most often the master calls this routine the shorter is the inactivity interval of the slaves.

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phq_init.f90, compute_becalp.f90

`phq_init.f90` computes the products `becp`

$$\langle \beta^{I}_{m} | \psi_{\mathbf{k}v\sigma} \rangle = \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{R}_{\ell}} \beta^{sm}_{\mathbf{k}v\sigma},$$

and `alphap`

$$\frac{\partial \langle \beta^{I}_{m}|}{\partial \mathbf{u}_{\alpha}(\ell, s)} | \psi_{\mathbf{k}v\sigma} \rangle = \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{R}_{\ell}} \alpha^{s\alpha m}_{\mathbf{k}v\sigma}.$$

`compute_becalp.f90` computes the products `becq`

$$\langle \beta^{I}_{m} | \psi_{\mathbf{k}+\mathbf{q}v\sigma} \rangle = \frac{1}{\sqrt{N}} e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_{\ell}} \beta^{sm}_{\mathbf{k}+\mathbf{q}v\sigma},$$

and `alpq`

$$\frac{\partial \langle \beta^{I}_{m}|}{\partial \mathbf{u}_{\alpha}(\ell, s)} | \psi_{\mathbf{k}+\mathbf{q}v\sigma} \rangle = \frac{1}{\sqrt{N}} e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_{\ell}} \alpha^{s\alpha m}_{\mathbf{k}+\mathbf{q}v\sigma}.$$

compute_weights.f90, compute_alphasum.f90, compute_becsum_ph.f90

`compute_weights.f90` computes the weights (saved in `wgg`) in the definition of ($i \rightarrow \mathbf{k}v$, $j \rightarrow \mathbf{k}+\mathbf{q}v'$)

$$|\delta^\mu \psi_{i\sigma}\rangle = \sum_j \left[\tilde{\theta}_{F,i\sigma}\theta_{i\sigma,j\sigma} + \tilde{\theta}_{F,j\sigma}\theta_{j\sigma,i\sigma}\right] |\psi_{j\sigma}\rangle\langle\psi_{j\sigma}|\frac{\partial S}{\partial \mu}|\psi_{i\sigma}\rangle.$$

`compute_alphasum.f90` computes:

$$c^{s\alpha\sigma}_{nm} = \frac{1}{N}\sum_{\mathbf{k}v} \tilde{\theta}_{F,\mathbf{k}v\sigma}\left[\alpha^{*s\alpha n}_{\mathbf{k}v\sigma}\beta^{sm}_{\mathbf{k}v\sigma} + \beta^{*sn}_{\mathbf{k}v\sigma}\alpha^{s\alpha m}_{\mathbf{k}v\sigma}\right].$$

`compute_becsum_ph.f90` computes:

$$b^{\sigma}_{snm} = \frac{1}{N}\sum_{\mathbf{k}v} \tilde{\theta}_{F,\mathbf{k}v\sigma}\beta^{*sn}_{\mathbf{k}v\sigma}\beta^{sm}_{\mathbf{k}v\sigma},$$

drho.f90

This routine computes the fourth part of the dynamical matrix:

$$\frac{d^2 F^{(4)}_{tot}}{d\mu d\lambda} = -\sum_{i\sigma} \left\{ \langle \delta^\mu \psi_{i\sigma} | \left[\frac{\partial V^\sigma_{KS}}{\partial \lambda} - \varepsilon_{i\sigma} \frac{\partial S}{\partial \lambda} \right] | \psi_{i\sigma} \rangle + (\mu \leftrightarrow \lambda) \right\}.$$

and the change of the charge due to the displacement of the augmentation charge:

$$\Delta^\mu \rho_\sigma(\mathbf{r}) = -\sum_i \langle \psi_{i\sigma} | K(\mathbf{r}) | \delta^\mu \psi_{i\sigma} \rangle + \sum_i \tilde{\theta}_{F,i\sigma} \langle \psi_{i\sigma} | \frac{\partial K(\mathbf{r})}{\partial \mu} | \psi_{i\sigma} \rangle$$

for all the modes and saves it on disk. This is done with the help of several routines.

drho.f90

Actually the quantity that is needed is the charge induced by a phonon perturbation of wavevector **q**:

$$\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\rho_\sigma(\mathbf{r}) = \sum_\ell e^{i\mathbf{q}\cdot\mathbf{R}_\ell}\Delta^{\mathbf{u}_\alpha(\ell,s)}\rho_\sigma(\mathbf{r})$$

so we define:

$$\delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}(\mathbf{r}) = \sum_\ell e^{i\mathbf{q}\cdot\mathbf{R}_\ell}\delta^{\mathbf{u}_\alpha(\ell,s)}\psi_{\mathbf{k}v\sigma}(\mathbf{r})$$

compute_drhous.f90

This is a driver that for each **k** point calls `incdrhous.f90` to accumulate two quantities needed to compute $\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\rho_\sigma(\mathbf{r})$.

$$\begin{aligned}\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\rho_\sigma(\mathbf{r}) &= \sum_{\mathbf{k}v} \psi^*_{\mathbf{k}v\sigma}(\mathbf{r})\delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}(\mathbf{r}) \\ &+ \sum_{\mathbf{k}v}\sum_{Inm} Q^{\gamma(I)}_{nm}(\mathbf{r}-\mathbf{R}_I)\langle\psi_{\mathbf{k}v\sigma}|\beta^I_n\rangle\langle\beta^I_m|\delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}\rangle \\ &+ \dots\end{aligned}$$

The first term is accumulated by `incdrhous.f90` directly, while the second is accumulated by `addusdbec.f90`

incdrhous.f90

This routine accumulates a part of $\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\rho_\sigma(\mathbf{r})$

$$\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\rho_\sigma(\mathbf{r}) = \sum_{\mathbf{k}v} \psi^*_{\mathbf{k}v\sigma}(\mathbf{r})\delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}(\mathbf{r}) + \dots$$

The rest is calculated by `drho.f90` calling `addusddens.f90` with `iflag=1`.

$$\begin{aligned}\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\rho_\sigma(\mathbf{r}) &= \dots + \sum_{\mathbf{k}v}\sum_{Inm} Q^{\gamma(I)}_{nm}(\mathbf{r}-\mathbf{R}_I)\langle\psi_{\mathbf{k}v\sigma}|\beta^I_n\rangle\langle\beta^I_m|\delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}\rangle \\ &+ \sum_{\ell} e^{i\mathbf{q}\cdot\mathbf{R}_\ell}\sum_{snm}\Bigg[Q^{\gamma(I)}_{nm}(\mathbf{r}-\mathbf{R}_I)c^{s\alpha\sigma}_{nm} \\ &+ \frac{\partial Q^{\gamma(I)}_{nm}(\mathbf{r}-\mathbf{R}_I)}{\partial \mathbf{u}_\alpha(\ell,s)} b^\sigma_{snm}\Bigg],\end{aligned}$$

incdrhous.f90

$|\delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}\rangle$ is calculated by this routine:

$$
\begin{aligned}
|\delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}\rangle &= \sum_{\ell} e^{i\mathbf{q}\mathbf{R}_\ell} |\delta^{\mathbf{u}_{\alpha}(\ell,s)}\psi_{\mathbf{k}v\sigma}\rangle \\
&= \sum_{v'} w_{\mathbf{k}v\sigma,\mathbf{k}+\mathbf{q}v'\sigma} \sum_{nm} q^{s}_{nm} \Big(\alpha^{*s\alpha n}_{\mathbf{k}+\mathbf{q}v'\sigma} \beta^{sm}_{\mathbf{k}v\sigma} \\
&+ \beta^{*sn}_{\mathbf{k}+\mathbf{q}v'\sigma} \alpha^{s\alpha m}_{\mathbf{k}v\sigma} \Big) |\psi_{\mathbf{k}+\mathbf{q}v'\sigma}\rangle \\
&= \sum_{v'} A^{\mathbf{u}_{s\alpha}(\mathbf{q})}_{\mathbf{k}v'v\sigma} |\psi_{\mathbf{k}+\mathbf{q}v'\sigma}\rangle
\end{aligned}
$$

addusddens.f90

When `(iflag=1)` this routine receives in `dbecsum`

$$d^{\mathbf{u}_{s\alpha}(\mathbf{q})\sigma}_{s_1 nm} = \frac{2}{N}\sum_{\mathbf{k}v} \beta^{*s_1 n}_{\mathbf{k}v\sigma} \delta^{\mathbf{u}_{s\alpha}(\mathbf{q})} \beta^{s_1 m}_{\mathbf{k}v\sigma},$$

where

$$\langle \beta^{I}_{m} | \delta^{\mathbf{u}_{s\alpha}(\mathbf{q})} \psi_{\mathbf{k}v\sigma} \rangle = \frac{1}{\sqrt{N}} e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_\ell} \delta^{\mathbf{u}_{s\alpha}(\mathbf{q})} \beta^{s_1 m}_{\mathbf{k}v\sigma}$$

and implements the expression written above.

dvanqq.f90

This routine computes four integrals.

$$1\ I_{nm}^{\mathbf{u}_\alpha(\ell,s)\sigma} = \int d^3r\ V^\sigma_{eff}(\mathbf{r}) \frac{\partial Q_{nm}^{\gamma(s)}(\mathbf{r}-\mathbf{R}_l)}{\partial \mathbf{u}_\alpha(\ell,s)},$$

$$2\ I_{lnm}^{\mathbf{u}_\alpha(\ell,s)} = \int d^3r\ \frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_\alpha(\ell,s)} Q_{nm}^{\gamma(l)}(\mathbf{r}-\mathbf{R}_l),$$

$$4\ I_{nm}^{\mathbf{u}_\alpha(\ell,s)\beta\sigma} = \int d^3r\ V^\sigma_{eff}(\mathbf{r}) \frac{\partial^2 Q_{nm}^{\gamma(s)}(\mathbf{r}-\mathbf{R}_l)}{\partial \mathbf{u}_\alpha(\ell,s)\partial \mathbf{u}_\beta(\ell,s)},$$

$$5\ I_{nm}^{\mathbf{u}_\alpha(\ell,s)\mathbf{u}_\beta(\ell',s')} = \int d^3r\ \frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_\alpha(\ell,s)}\ \frac{\partial Q_{nm}^{\gamma(s')}(\mathbf{r}-\mathbf{R}_{l'})}{\partial \mathbf{u}_\beta(\ell',s')}.$$

dvanqq.f90

In previous equation:

$$ {}^{1}I_{nm}^{\mathbf{u}_\alpha(\ell,s)\sigma} = {}^{1}I_{nm}^{*s\alpha\sigma} $$

$$ {}^{2}I_{lnm}^{\mathbf{u}_\alpha(\ell,s)} = \frac{1}{N}\sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot(\mathbf{R}_\ell-\mathbf{R}_{\ell_1})}\ {}^{2}I_{s_1 nm}^{s\alpha\mathbf{q}} $$

$$ {}^{4}I_{nm}^{\mathbf{u}_\alpha(\ell,s)\beta\sigma} = {}^{4}I_{nm}^{s\alpha\beta\sigma} $$

$$ {}^{5}I_{nm}^{\mathbf{u}_\alpha(\ell,s)\mathbf{u}_\beta(\ell_1,s_1)} = \frac{1}{N}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}_\ell-\mathbf{R}_{\ell_1})}\ {}^{5}I_{nm}^{ss_1\alpha\beta\mathbf{q}} $$

compute_nldyn.f90

This routine computes

$$\frac{d^2 F^{(4)}_{tot}}{d\mu d\lambda} = -\sum_{i\sigma} \left\{ \langle \delta^\mu \psi_{i\sigma} | \left[\frac{\partial \bar{V}^\sigma_{KS}}{\partial \lambda} - \varepsilon_{i\sigma} \frac{\partial S}{\partial \lambda} \right] |\psi_{i\sigma}\rangle + (\mu \leftrightarrow \lambda) \right\}.$$

Note that the term computed by `drho.f90` should have $\frac{\partial V^\sigma_{KS}}{\partial \lambda}$. Here the bar on V^σ_{KS} indicates that a part is not calculated by this routine but in `drho.f90`. This part is:

$$-\sum_{i\sigma} \int d^3r \, \frac{dV_{loc}(\mathbf{r})}{d\lambda} \psi_{i\sigma}(\mathbf{r}) \delta^\mu \psi^*_{i\sigma}(\mathbf{r}),$$

compute_nldyn.f90

We have

$$\frac{d^2 F^{(4)}_{tot}}{d\mu d\lambda} = - \sum_{i\sigma} \sum_{lnm} \Big\{ D^{eff,l\sigma}_{nm} \langle \delta^\mu \psi_{i\sigma} | \frac{\partial \beta^l_n}{\partial \lambda} \rangle \langle \beta^l_m | \psi_{i\sigma} \rangle + D^{eff,l\sigma}_{nm} \langle \delta^\mu \psi_{i\sigma} | \beta^l_n \rangle \langle \frac{\partial \beta^l_m}{\partial \lambda} | \psi_{i\sigma} \rangle + {}^2 I^\lambda_{lnm} \langle \delta^\mu \psi_{i\sigma} | \beta^l_n \rangle \langle \beta^l_m | \psi_{i\sigma} \rangle + {}^1 I^{\lambda\sigma}_{lnm} \langle \delta^\mu \psi_{i\sigma} | \beta^l_n \rangle \langle \beta^l_m | \psi_{i\sigma} \rangle + (\mu \leftrightarrow \lambda) \Big\},$$

where we defined $D^{eff,l\sigma}_{mn} = D^{l\sigma}_{mn} - \varepsilon_{i\sigma} q^l_{mn}$.

compute_nldyn.f90

In terms of the quantities defined above we can write:

$$\begin{aligned}
\langle \delta^{\mathbf{u}_{s\alpha}(\mathbf{q})} \psi_{\mathbf{k}v\sigma}| &= \sum_{l} e^{-i\mathbf{q}\mathbf{R}_\ell} \langle \delta^{\mathbf{u}_\alpha(\ell,s)} \psi_{\mathbf{k}v\sigma}| \\
&= \sum_{v'} w_{\mathbf{k}v\sigma,\mathbf{k}+\mathbf{q}v'\sigma} \sum_{mn} q^{s}_{mn} \Big(\beta^{*sn}_{\mathbf{k}v\sigma} \alpha^{s\alpha m}_{\mathbf{k}+\mathbf{q}v'\sigma} \\
&+ \alpha^{*s\alpha n}_{\mathbf{k}v\sigma} \beta^{sm}_{\mathbf{k}+\mathbf{q}v'\sigma} \Big) \langle \psi_{\mathbf{k}+\mathbf{q}v'\sigma}| \\
&= \sum_{v'} A^{*\mathbf{u}_{s\alpha}(\mathbf{q})}_{\mathbf{k}v'v\sigma} \langle \psi_{\mathbf{k}+\mathbf{q}v'\sigma}|
\end{aligned}$$

compute_nldyn.f90

So that the expression calculated by this routine is:

$$\begin{aligned}
\Phi_{\alpha\beta}\left(\mathbf{q}, s, s'\right) = & - \frac{1}{N} \sum_{\mathbf{k}\sigma} \sum_{vv'} \sum_{nm} \Big\{ A^{*\mathbf{u}_{s\alpha}(\mathbf{q})}_{\mathbf{k}v'v\sigma} D^{eff,s'\sigma}_{nm} \alpha^{*s'\beta n}_{\mathbf{k}+\mathbf{q}v'\sigma} \beta^{s'm}_{\mathbf{k}v\sigma} \\
& + A^{*\mathbf{u}_{s\alpha}(\mathbf{q})}_{\mathbf{k}v'v\sigma} D^{eff,s'\sigma}_{nm} \beta^{*s'n}_{\mathbf{k}+\mathbf{q}v'\sigma} \alpha^{s'\beta m}_{\mathbf{k}v\sigma} \\
& + A^{*\mathbf{u}_{s\alpha}(\mathbf{q})}_{\mathbf{k}v'v\sigma} \sum_{s_1} {}^2 I^{s'\beta\mathbf{q}}_{s_1 nm} \beta^{*s_1 n}_{\mathbf{k}+\mathbf{q}v'\sigma} \beta^{s_1 m}_{\mathbf{k}v\sigma} \\
& + A^{*\mathbf{u}_{s\alpha}(\mathbf{q})}_{\mathbf{k}v'v\sigma} {}^1 I^{s'\beta\sigma}_{nm} \beta^{*s'n}_{\mathbf{k}+\mathbf{q}v'\sigma} \beta^{s'm}_{\mathbf{k}v\sigma} \Big\} + h.c.,
\end{aligned}$$

The hermitean conjugate (h.c.) is added in `drho.f90`.

dynmat_us.f90

This routine computes directly a part of the term:

$$\frac{d^2 F^{(1)}_{tot}}{d\mu d\lambda} = \sum_{i\sigma} \tilde{\theta}_{F,i\sigma} \langle \psi_{i\sigma} | \left[\frac{\partial^2 V^{\sigma}_{KS}}{\partial\mu\partial\lambda} - \varepsilon_{i\sigma} \frac{\partial^2 S}{\partial\mu\partial\lambda} \right] | \psi_{i\sigma} \rangle,$$

in particular the part similar to the norm conserving potential that corresponds to:

$$\frac{\partial^2 V^{\sigma}_{KS}(\mathbf{r}_1, \mathbf{r}_2)}{\partial\mu\partial\lambda} = \frac{\partial^2 V_{NL}(\mathbf{r}_1, \mathbf{r}_2)}{\partial\mu\partial\lambda} + \int d^3r \, \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial\mu\partial\lambda} K(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2) + \dots$$

and calls `addusdynmat.f90` to compute the rest.

addusdynmat.f90

This routine computes the rest of the term $\frac{d^2 F^{(1)}_{tot}}{d\mu d\lambda}$. In particular the part that corresponds to the terms:

$$\frac{\partial^2 V^{\sigma}_{KS}(\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu\partial\lambda} = \cdots + \int d^3r\ V^{\sigma}_{eff}(\mathbf{r}) \frac{\partial^2 K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu\partial\lambda} + \left[\int d^3r\ \frac{\partial V_{loc}(\mathbf{r})}{\partial\lambda} \frac{\partial K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2)}{\partial\mu} + (\lambda \leftrightarrow \mu)\right].$$

that can be written in terms of the four integrals calculated by `dvanqq.f90`

addusdynmat.f90

The two terms calculated by this routine can be written in terms of the previous four integrals and of the quantities computed by `compute_alphasum.f90` and `compute_becsum.f90`.

$$
\begin{aligned}
\Phi^{(1b)}_{\alpha\beta}(\mathbf{q}, s, s') &= \delta_{ss'} \Bigg\{ \sum_{\sigma} \sum_{nm} {}^{4}I^{s\alpha\beta\sigma}_{nm} \, b^{s\sigma}_{nm} \\
&+ \left[\sum_{\sigma} \sum_{nm} {}^{1}I^{*s\alpha\sigma}_{nm} \, c^{s\beta\sigma}_{nm} + (\alpha \leftrightarrow \beta) \right] \Bigg\},
\end{aligned}
$$

$$
\Phi^{(1c)}_{\alpha\beta}(\mathbf{q}, s, s') = \Bigg\{ \left[\sum_{\sigma} \sum_{nm} {}^{5}I^{ss'\alpha\beta\mathbf{q}}_{nm} \, b^{s'\sigma}_{nm} + \sum_{\sigma} \sum_{nm} {}^{2}I^{*s\alpha\mathbf{q}}_{s'nm} \, c^{s'\beta\sigma}_{nm} \right] + h.c. \Bigg\}.
$$

dvqpsi_us_only.f90

Computes a part of the right-hand side of the linear system:

$$\left[\frac{dV^{\sigma}_{NL}}{d\mu} - \varepsilon_{i\sigma}\frac{\partial S}{\partial \mu}\right]|\psi_{i\sigma}\rangle$$

The contribution of the local potential is calculated in `dvqpsi_us.f90`, the contribution of $\frac{dV^{\sigma}_{Hxc}(\mathbf{r})}{d\mu}$ is calculated in `solve_linter.f90` while an additional US part is calculated in `adddvscf.f90`.

dvqpsi_us_only.f90

This routine computes the following term:

$$
\begin{aligned}
\left[\frac{\partial V^{\sigma}_{NL}}{\partial \mu} - \varepsilon_{i\sigma}\frac{\partial S}{\partial \mu}\right]|\psi_{i\sigma}\rangle \quad = \quad & \sum_{lmn} \Bigg\{ D^{eff,l\sigma}_{nm} |\frac{\partial \beta^l_n}{\partial \lambda}\rangle\langle\beta^l_m|\psi_{i\sigma}\rangle \\
+ \quad & D^{eff,l\sigma}_{nm} |\beta^l_n\rangle\langle\frac{\partial \beta^l_m}{\partial \lambda}|\psi_{i\sigma}\rangle \\
+ \quad & {}^2 I^{\lambda}_{lnm} |\beta^l_n\rangle\langle\beta^l_m|\psi_{i\sigma}\rangle \\
+ \quad & {}^1 I^{\lambda\sigma}_{lnm} |\beta^l_n\rangle\langle\beta^l_m|\psi_{i\sigma}\rangle \Bigg\}
\end{aligned}
$$

newdq.f90

This routine computes the following integral:

$$ {}^{3}I^{\mu\sigma}_{Inm} = \int d^3r \, \frac{dV^{\sigma}_{Hxc}(\mathbf{r})}{d\mu} \, Q^{\gamma(I)}_{nm}(\mathbf{r} - \mathbf{R}_I), $$

and is called by `solve_linter.f90` after computing a new estimate of $\frac{dV^{\sigma}_{Hxc}(\mathbf{r})}{d\mu}$. Defining:

$$ {}^{3}I^{\mathbf{u}_{s\alpha}(\mathbf{q})\sigma}_{I_1 nm} = \sum_{\ell} e^{i\mathbf{q}\cdot\mathbf{R}_\ell} \; {}^{3}I^{\mathbf{u}_{\alpha}(\ell,s)\sigma}_{I_1 nm} $$

we have

$$ {}^{3}I^{\mathbf{u}_{s\alpha}(\mathbf{q})\sigma}_{I_1 nm} = e^{i\mathbf{q}\cdot\mathbf{R}_{\ell_1}} \; {}^{3}I^{\mathbf{u}_{s\alpha}(\mathbf{q})\sigma}_{s_1 nm} $$

adddvscf.f90

This routine computes the part of the right-hand side of the linear system

$$\int d^3r \, \frac{dV^{\sigma}_{Hxc}(\mathbf{r})}{d\mu} \left[K(\mathbf{r};\mathbf{r}_1,\mathbf{r}_2) - \delta(\mathbf{r}-\mathbf{r}_1)\delta(\mathbf{r}-\mathbf{r}_2)\right] |\psi_{i\sigma}\rangle =$$

Using the integral ${}^3I^{\mu\sigma}_{lnm}$ computed by `newdq.f90`. Expanding we have:

$$= \sum_{lmn} {}^3I^{\mu\sigma}_{lnm} |\beta^l_m\rangle\langle\beta^l_n|\psi_{i\sigma}\rangle$$

and the implemented term is:

$$\sum_{s_1}\sum_{nm} {}^3I^{\mathbf{u}_{s\alpha}(\mathbf{q})\sigma}_{s_1 nm} \beta^{\gamma(s_1)}_n(\mathbf{k}+\mathbf{q}+\mathbf{G}) e^{-i(\mathbf{k}+\mathbf{q}+\mathbf{G})\cdot\tau_{s_1}} \beta^{s_1 m}_{\mathbf{k}v\sigma}$$

incdrhoscf.f90, addusdbec.f90

`incdrhoscf.f90` accumulates for each **k**

$$2\,\mathrm{Re}\sum_i \psi_{i\sigma}(\mathbf{r})^*\tilde{\Delta}^\mu\psi_{i\sigma}(\mathbf{r})$$

as in the norm conserving case, while `addusdbec.f90` accumulates the term

$$a_{s_1 nm}^{\mathbf{u}_{s\alpha}(\mathbf{q})\sigma} = \frac{2}{N}\sum_{\mathbf{k}v} \beta_{\mathbf{k}v\sigma}^{*s_1 n}\tilde{\Delta}^{\mathbf{u}_{s\alpha}(\mathbf{q})}\beta_{\mathbf{k}v\sigma}^{s_1 m},$$

that is used by `addusddens.f90` to calculate the augmentation part.

addusddens.f90

This routine (called with `iflag=0`) computes:

$$\frac{d\rho_\sigma(\mathbf{r})}{d\mu} = 2\,\mathrm{Re}\sum_i \langle\psi_{i\sigma}|\,[K(\mathbf{r})-1]\,|\tilde{\Delta}^\mu\psi_{i\sigma}\rangle + \dots$$

$$= 2\sum_{\mathbf{k}v}\sum_{Inm} Q_{nm}^{\gamma(I)}(\mathbf{r}-\mathbf{R}_I)\langle\psi_{\mathbf{k}v\sigma}|\beta_n^I\rangle\langle\beta_m^I|\tilde{\Delta}^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}\rangle + \dots$$

using the quantity accumulated by `addusdbec.f90`. Reads from disk $\Delta^\mu\rho_\sigma(\mathbf{r})$ and adds it to $\frac{d\rho_\sigma(\mathbf{r})}{d\mu}$.

drhodvus.f90

After computing the induced potential this routine computes the term of the dynamical matrix that is obtained from:

$$\frac{d^2 F_{tot}^{(3)}}{d\mu d\lambda} = \sum_\sigma \int d^3r \, \frac{dV^\sigma_{Hxc}(\mathbf{r})}{d\mu} \Delta^\lambda \rho_\sigma(\mathbf{r}),$$

where $\Delta^\lambda \rho_\sigma(\mathbf{r})$ is read from disk. In the dynamical matrix this term is actually:

$$\Phi^{(3)}_{\alpha\beta}(\mathbf{q}, s, s') = \sum_\sigma \int_\Omega d^3r \, \frac{dV^{*\sigma}_{Hxc}(\mathbf{r})}{d\mathbf{u}_{s\alpha}(\mathbf{q})} \Delta^{\mathbf{u}_{s'\beta}(\mathbf{q})} \rho_\sigma(\mathbf{r}),$$

drhodv.f90

This routine needs a few generalizations. It must calculate

$$\frac{d^2 F^{(2)}_{tot}}{d\mu d\lambda} = 2\,\mathrm{Re}\sum_{i\sigma} \langle \Delta^\mu \psi_{i\sigma}| \left[\frac{\partial V^\sigma_{KS}}{\partial\lambda} - \varepsilon_{i\sigma}\frac{\partial S}{\partial\lambda}\right] |\psi_{i\sigma}\rangle,$$

which is a term similar to that computed by `compute_nldyn.f90` with $\langle \Delta^\mu \psi_{i\sigma}|$ instead of $\langle \delta^\mu \psi_{i\sigma}|$. The contribution of the local potential is similar to the norm conserving case and calculated in `drhodvloc.f90`. We need the two products `becpq`:

$$\langle \beta^{I_1}_m | \Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})} \psi_{\mathbf{k}v\sigma}\rangle = \frac{1}{\sqrt{N}} e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_{\ell_1}} \Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\beta^{s_1 m}_{\mathbf{k}v\sigma}$$

and `dalpq`

$$\frac{\partial\langle \beta^{I'}_m|}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} |\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\psi_{\mathbf{k}v\sigma}\rangle = \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{R}_{\ell'}} \Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\alpha^{s'\beta m}_{\mathbf{k}v\sigma}.$$

drhodvnl.f90

In analogy with `compute_nldyn.f90`

$$
\begin{aligned}
\frac{d^2 F^{(4)}_{tot}}{d\mu d\lambda} &= 2 \sum_{i\sigma} \sum_{lmn} \Big\{ D^{eff,l\sigma}_{nm} \langle \Delta^\mu \psi_{i\sigma} | \frac{\partial \beta^l_n}{\partial \lambda} \rangle \langle \beta^l_m | \psi_{i\sigma} \rangle \\
&+ D^{eff,l\sigma}_{nm} \langle \Delta^\mu \psi_{i\sigma} | \beta^l_n \rangle \langle \frac{\partial \beta^l_m}{\partial \lambda} | \psi_{i\sigma} \rangle \\
&+ {}^2 I^\lambda_{lnm} \langle \Delta^\mu \psi_{i\sigma} | \beta^l_n \rangle \langle \beta^l_m | \psi_{i\sigma} \rangle \\
&+ {}^1 I^{\lambda\sigma}_{lnm} \langle \Delta^\mu \psi_{i\sigma} | \beta^l_n \rangle \langle \beta^l_m | \psi_{i\sigma} \rangle \Big\}
\end{aligned}
$$

drhodvnl.f90

In analogy with `compute_nldyn.f90`

$$\begin{aligned}
\Phi^{(2)}_{\alpha\beta}(\mathbf{q},s,s') &= \frac{2}{N}\sum_{\mathbf{k}v\sigma}\sum_{mn}\Big\{ D^{eff,s'\sigma}_{nm}\big(\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\alpha^{*s'\beta n}_{\mathbf{k}v\sigma}\big)\beta^{s'm}_{\mathbf{k}v\sigma} \\
&+ D^{eff,s'\sigma}_{nm}\big(\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\beta^{*s'n}_{\mathbf{k}v\sigma}\big)\alpha^{s'\beta m}_{\mathbf{k}v\sigma} \\
&+ \sum_{s_1} {}^{2}I^{s'\beta\mathbf{q}}_{s_1 nm}\big(\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\beta^{*s_1 n}_{\mathbf{k}v\sigma}\big)\beta^{s_1 m}_{\mathbf{k}v\sigma} \\
&+ {}^{1}I^{s'\beta\sigma}_{nm}\big(\Delta^{\mathbf{u}_{s\alpha}(\mathbf{q})}\beta^{*s'n}_{\mathbf{k}v\sigma}\big)\beta^{s'm}_{\mathbf{k}v\sigma}\Big\},
\end{aligned}$$

where we used the time reversal symmetry.

PAW - drho.f90, addusddens.f90

In `drho.f90`, the call to `addusddens.f90` with `iflag=1` and the variable `dbecsum` that contains:

$$\sum_i \langle \psi_{i,\sigma} | \beta^I_m \rangle \langle \beta^I_n | \delta^\mu \psi_{i,\sigma} \rangle,$$

saves in `becsumort` the quantity

$$\begin{aligned} b^{\sigma,\mu}_{I,mn} &= \sum_i \tilde{\theta}_{F,i\sigma} \langle \psi_{i,\sigma} | \frac{\partial \left(|\beta^I_m\rangle\langle\beta^I_n| \right)}{\partial \mu} | \psi_{i,\sigma} \rangle \\ &- \sum_i \langle \psi_{i,\sigma} | \beta^I_m \rangle \langle \beta^I_n | \delta^\mu \psi_{i,\sigma} \rangle. \end{aligned}$$

All the modes are calculated in `drho.f90`.

PAW_dusymmetrize, PAW_dpotential

In `solve_linter.f90`:

$$\frac{d\rho^{I,\sigma}_{mn}}{d\mu} = 2Re\sum_i \langle\psi_{i,\sigma}|\beta^I_m\rangle\langle\beta^I_n|\Delta^\mu\psi_{i,\sigma}\rangle + b^{\sigma,\mu}_{I,mn}.$$

`becsumort` is added to the first term contained in `dbecsum`. $\frac{d\rho^{I,\sigma}_{mn}}{d\mu}$ is symmetrized in `PAW_dusymmetrize`.

$$\frac{dD^{1,\sigma}_{I,mn}}{d\mu} = \sum_{\sigma_1}\int_{\Omega_I} d^3r\ \Phi^{I,AE}_m(\mathbf{r})\Phi^{I,AE}_n(\mathbf{r})\frac{dV^{I,\sigma}_{eff}}{d\rho^{1,I}_{\sigma_1}}\frac{d\rho^{1,I}_{\sigma_1}}{d\mu}.$$

and $\frac{d\tilde{D}^{1,\sigma}_{I,mn}}{d\mu}$ are calculated by `PAW_dpotential`. These routines are in `PAW_onecenter.f90` and `PAW_symmetry.f90`.

PAW - drhodvus.f90

This routine is called after the calculation of $\Delta D^{1,\sigma,\mu}_{I,mn}$. It has it in the variable `int3_paw` and computes

$$\frac{d^2 E^{(3)}_{tot}}{d\mu d\lambda} = \frac{d^2 E^{(3)US}_{tot}}{d\mu d\lambda} + \sum_{\sigma} \sum_{I,mn} \Delta D^{1,\sigma,\mu}_{I,mn} b^{\sigma,\lambda}_{I,mn}.$$