Coulomb Matrix in localized basis: How to deal with singularity in extended systems

Maria Dragoumi

Cafee Talk,
July 2019

Total energy MP2 and Single Particle Energies MP2 and D2 with FHI-aims

Second order MBPT on FHI-aims for extended systems

SPE from 2nd order Møller Plesset perturbation theory (SPE-MP2)

→ Beyond independent particle approximation

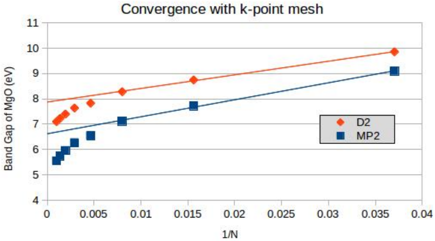
→ First step towards the exact solution

→Self-correlation free (Second-order exchange)

Second order (self-energy) Dyson equation (D2)

→ Scale as MP2 but goes beyond (Dyson equation (D2))

What went wrong:



What is the difference with other approximations?

- LDA, GGA etc.:
  Coulomb potential not explicitly take into account: single-particle effective potential

$$V_{eff}(\vec{r})$$

- HF, MBPT, GW, RPA etc.:
  Coulomb potential taken into account: two-particle Coulomb operator

$$V(\vec{r}, \vec{r'}) = \frac{1}{|\vec{r} - \vec{r'}|}$$

- Hybrid functionals:
  Screened coulomb operator

$$V(\vec{r}, \vec{r'}) = \frac{e^{-a|\vec{r} - \vec{r'}|}}{|\vec{r} - \vec{r'}|}$$

Matrix elements of the Coulomb potential Operator

$$V_{ab,cd} =< i,j|\widehat{V}|k,l >= \int d\vec{r} \int d\vec{r'} \frac{\phi_i^*(\vec{r})\phi_j^*(\vec{r'})\phi_k(\vec{r})\phi_l(\vec{r'})}{|\vec{r}-\vec{r'}|}$$

Coulomb operator in Plane Wave Basis $\phi_{k\sigma} = \frac{1}{V^{\frac{1}{2}}} e^{i\vec{k}\cdot\vec{r}}\chi(\sigma)$

$$V_{\vec{k}\sigma_1\vec{k'}\sigma_2,\vec{q}\sigma_3\vec{q'}\sigma_4} = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\delta_{\vec{k}+\vec{k'}+\vec{G},\vec{q}+\vec{q'}} \frac{4\pi}{V} \frac{1}{|\vec{G}+\vec{k}-\vec{q}|^2}$$

- The Coulomb potential is singular for $\vec{G}=0$ when $\vec{k}-\vec{q}=\delta\vec{k}\rightarrow 0$.

$\rightarrow$For a localized basis set the coulomb matrix is more complicated but also singular for $\vec{G}=0$ with the leading term: $\propto 1/|\delta\vec{k}|^2$

Coulomb Matrix in FHI-aims

Bloch orbitals from localized basis: $\phi_{a\vec{k}\sigma}(\vec{r}) = \sum_R e^{i\vec{k}\cdot\vec{R}} \phi_{a\sigma}(\vec{r} - \vec{R})$

Auxiliary basis set $P_\mu^{\vec{k}}(\vec{r})$ for the product of the wave functions:

$$\phi^*_{a\vec{k}\sigma}(\vec{r})\phi_{c\vec{q}\sigma}(\vec{r}) = \sum_\mu C^\mu_{ac,\sigma}(\vec{k},\vec{q}) P_\mu^{\vec{k}-\vec{q}}(\vec{r})$$

where: $P_\mu^{\vec{k}}(\vec{r}) = \sum_R e^{i\vec{k}\cdot\vec{R}} p_{\mu(l,m)}(\vec{r} - \vec{R}) Y_{lm}(\theta,\varphi)$

When we have two HF (or KS) states we can write:

$$\psi_{a\vec{k}\sigma}(\vec{r})\psi_{b\vec{k'}\sigma'}(\vec{r}) = \frac{1}{N_{\vec{R}}} \sum_\mu \sum_{lm} M^{\mu lm}_{a\vec{k}\sigma, b\vec{k'}\sigma'} P^{\vec{k}-\vec{k'}}_{\mu lm}(\vec{r})$$

where: $M^{\mu lm}_{a\vec{k}\sigma, b\vec{q}\sigma'} = \sum_{ij} c_{ia,\sigma} c_{jb,\sigma} C^\mu_{ij}(\vec{k},\vec{q})$

Coulomb matrix in the auxiliary base $P_{\mu}^{\vec{k}}(\vec{r})$ is:

$$V_{\mu,\mu'}(\vec{k}-\vec{q},-\vec{k'}+\vec{q'}) = \delta_{\vec{k}+\vec{k'},\vec{q}+\vec{q'}} \frac{1}{N_{\vec{R}}} \sum_{\vec{R}} e^{i(\vec{k}-\vec{q})\vec{R}} \int d\vec{r} \int d\vec{r'} \frac{P_{\mu'}(\vec{r}-\vec{R})P_{\mu}(\vec{r'})}{|\vec{r}-\vec{r'}|}$$

Multipole-expansion for non-overlap:

$$V_{far} \sim (-1)^{l'+m'} Q_{\mu l} Q_{\mu' l'} C_{l'm',lm} \sum_{\vec{R}}^{far} e^{i(\vec{k}-\vec{q})\vec{R}} \frac{Y_{l+l'}^{m'-m}(\widehat{R})}{R^{l+l'+1}}$$

$Q_{\mu l}$: multipole moments

With Ewald sumation we get a term:

$$\propto \sum_{\vec{G}} Y_{l+l'}^{m'-m}(\widehat{e}_{\vec{G}+\vec{k}-\vec{q}}) \frac{e^{i\vec{R}_a(\vec{G}+\vec{k}-\vec{q})-\eta^2|\vec{G}+\vec{k}-\vec{q}|^2}}{|\vec{G}+\vec{k}-\vec{q}|^{2-l-l'}}$$

$\rightarrow$Singular for $\vec{G}=0$ with the leading term: $\propto 1/|\delta\vec{k}|^2$ for $l+l'<2$: $l_{tot}=0$ (monopole-monopole) and $l_{tot}=1$ (monopole-dipole) terms.

How to deal with the singularity

What we realized: Each method needs a careful numerical treatment of the Brillouin zone integrals (different integrand)!

Hartree-Fock:

Exchange energy:

$$E^x = -\frac{1}{2}\sum_{ij,\sigma}^{occ}\int_{1BZ} d\vec{k}d\vec{q}\sum_{\mu\mu'} M^{\mu}_{i\vec{k}\sigma,j\vec{q}\sigma} M^{\mu'}_{j\vec{q}\sigma,i\vec{k}\sigma} V_{\mu,\mu'}(\delta\vec{k})$$

1st order (V^1): integrable singularity

Separate the potential: $V_{\mu,\mu'}(\delta\vec{k}) = V^{sing}_{\mu,\mu'}(\delta\vec{k}) + V^{finite}_{\mu,\mu'}(\delta\vec{k})$

$\rightarrow$ Singular part needs numerical treatment

Numerical treatment in HF

$\rightarrow$Gygi-Baldereschy Method:
Add and subtract a reference term which has the same singularities:

$$\int d\delta\vec{k}\frac{f(\delta\vec{k})}{|\delta\vec{k}|^2} = \int d\delta\vec{k}\left(\frac{f(\delta\vec{k})}{|\delta\vec{k}|^2} - f(0)G(\delta\vec{k})\right) + f(0)\int d\vec{k}G(\delta\vec{k})$$

$G(\delta\vec{k}) = \frac{e^{\gamma|\delta\vec{k}|}}{|\delta\vec{k}|^2}$

- Close to $\frac{1}{|\delta\vec{k}|^2}$ for small $\delta\vec{k}$
- Integrable analytically

Then we can approximate:

$$\int d\delta\vec{k}\frac{f(\delta\vec{k})}{|\delta\vec{k}|^2} = \sum_{\delta\vec{k}}{}'\left(\frac{f(\delta\vec{k})}{|\delta\vec{k}|^2} - f(0)G(\delta\vec{k})\right) + f(0)\int d\vec{k}G(\delta\vec{k})$$

Numerical treatment in HF

$\rightarrow$Cut Coulomb method:
Replace Coulomb potential with cut Coulomb potential.

- In reciprocal space: Replace $\frac{1}{|\delta\vec{k}|^2}$ with $\frac{1}{|\delta\vec{k}|^2}[1 - cos(R_c|\delta\vec{k}|)]$.
- In real space (also in FHI-aims):
  $V_{cut}(\vec{r} - \vec{r'}) = \frac{1}{|\vec{r} - \vec{r'}|}$ if $|\vec{r} - \vec{r'}| < R_c$, 0 otherwise

In the former implementation of MP2:

- Cut-Coulomb operator only for the Gamma point
- Full Coulomb operator for the rest of the k points

$\rightarrow$ SPE-MP2 do not converge properly if we use the same strategy.

Why?

Singularity treatment in SPE-MP2

SPE-MP2

Correction to single particle energies:

$$\epsilon^{(2)}_{n\vec{k}\sigma} = \frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\int d\vec{k'}d\vec{q}d\vec{q'}\frac{1}{\epsilon^{a\vec{q}\sigma,b\vec{q'}\sigma'}_{n\vec{k}\sigma,i\vec{k'}\sigma'}}\Bigg[\Big(\sum_{\mu\mu'}M^{\mu}_{n\vec{k}\sigma,a\vec{q}\sigma}M^{\mu'}_{i\vec{k'}\sigma',b\vec{q'}\sigma'}V_{\mu,\mu'}(\delta\vec{k})\Big)^2 +$$

$$\delta_{\sigma,\sigma}\Big(\sum_{\mu\mu'}M^{\mu}_{n\vec{k}\sigma,a\vec{q}\sigma}M^{\mu'}_{i\vec{k'}\sigma',b\vec{q'}\sigma'}V_{\mu,\mu'}(\delta\vec{k})\Big)\Big(\sum_{\mu\mu'}M^{\mu}_{n\vec{k}\sigma,b\vec{q'}\sigma'}M^{\mu'}_{i\vec{k'}\sigma',a\vec{q}\sigma}V_{\mu,\mu'}(\delta\vec{k})\Big)\Bigg]$$

$$\frac{1}{2}\sum_{\sigma'}\sum_{i,j,a}\int d\vec{k'}d\vec{q}d\vec{q'}\frac{1}{\epsilon^{i\vec{q}\sigma,j\vec{q'}\sigma'}_{n\vec{k}\sigma,a\vec{k'}\sigma'}}\Bigg[\Big(\sum_{\mu\mu'}M^{\mu}_{n\vec{k}\sigma,i\vec{q}\sigma}M^{\mu'}_{a\vec{k'}\sigma',j\vec{q'}\sigma'}V_{\mu,\mu'}(\delta\vec{k})\Big)^2 +$$

$$\delta_{\sigma,\sigma}\Big(\sum_{\mu\mu'}M^{\mu}_{n\vec{k}\sigma,i\vec{q}\sigma}M^{\mu'}_{a\vec{k'}\sigma',j\vec{q'}\sigma'}V_{\mu,\mu'}(\delta\vec{k})\Big)\Big(\sum_{\mu\mu'}M^{\mu}_{n\vec{k}\sigma,j\vec{q'}\sigma'}M^{\mu'}_{a\vec{k'}\sigma',i\vec{q}\sigma}V_{\mu,\mu'}(\delta\vec{k})\Big)\Bigg]$$

Potential: $V_{\mu,\mu'}(\delta\vec{k}) = V^{singular}_{\mu,\mu'}(\delta\vec{k}) + V^{finite}_{\mu,\mu'}(\delta\vec{k})$

Integrand $\sim (V^{singular})^2 + 2V^{singular}V^{finite} + (V^{finite})^2$

$(V^{singular})^2 \propto 1/|\delta\vec{k}|^4$

Coulomb matrix for non-overlap:

$$\propto \sum_{\vec{G}} Y_{l+l'}^{m'-m}(\widehat{e}_{\vec{G}+\vec{k}-\vec{q}}) \frac{e^{i\vec{R}_a(\vec{G}+\vec{k}-\vec{q})-\eta^2|\vec{G}+\vec{k}-\vec{q}|^2}}{|\vec{G}+\vec{k}-\vec{q}|^{2-l-l'}}$$

- Singular when $l + l' < 2$: $l_{tot} = 0$ (monopole-monopole), $l_{tot} = 1$ (monopole-dipole) terms.
- Monopole moment of two HF(KS) states for $\delta\vec{k} = 0$:

$$\mathcal{Q}_{l=0} = \int d\vec{r}\psi_{a\vec{k}\sigma}(\vec{r})\psi_{i\vec{k}\sigma'}(\vec{r}-\vec{R}) = \delta_{a\sigma,i\sigma'} \quad (1)$$

  from orthogonality of the HF(KS) orbitals.
- Total energy MP2: always pairs of unoccupied and occupied orbitals $\rightarrow$monopole term always zero.
- SPE-MP2: there is one non-zero monopole pair!
  Singular term $\propto 1/|\delta\vec{k}|$, integrable even for V^2

Needs numerical treatment!

Generalization of Gygi-Baldereschi method

$$\int d\delta\vec{k}\frac{f(\delta\vec{k})}{|\delta\vec{k}|^2} = \int d\delta\vec{k}\left(\frac{f(\delta\vec{k})}{|\delta\vec{k}|^2} - f(0)G(\delta\vec{k})\right) + f(0)\int d\vec{k}G(\delta\vec{k})$$

Implementation difficulties:

- Calculate correction for V^2 not for V like HF (as is implemented now)
- Form of $f(\delta\vec{k})$ much more complicated than HF

With a little hard work it should be soon implemented!

Then FHI-aims will calculate:

- Relatively fast corrections to HF spectrum with correlation (SPE-MP2)
- Accurate correction to HF single-particle energies from renormalized MP2 (D2)

This analysis can be useful to other methods!

Thank you

Appendix

Equations of Generalized Gygi-Baldereschi method

For Hartree-Fock: (Note the momentum conservation: $\vec{q} = \vec{k} - \delta\vec{k}$)

$$
\begin{aligned}
E^x = & -\frac{1}{2}\sum_{mn,\sigma}^{occc}\int_{1BZ} d\vec{k}d\delta\vec{k}\sum_{\mu\mu'} M^{\mu}_{n\sigma,m\sigma}(\vec{k},\vec{q})M^{\mu'}_{m\sigma,n\sigma}(\vec{k},\vec{q})V^{finite}_{\mu,\mu'}(\delta\vec{k}) + \\
& + \frac{1}{2}\sum_{mn,\sigma}^{occ}\int_{1BZ} d\vec{k}d\delta\vec{k}\Big[\sum_{\mu\mu'} M^{\mu}_{n\sigma,m\sigma}(\vec{k},\vec{q})M^{\mu'}_{m\sigma,n\sigma}(\vec{k},\vec{q})V^{sing}_{\mu,\mu'}(\delta\vec{k}) - \\
& - \sum_{\mu\mu'} M^{\mu}_{n\sigma,m\sigma}(\vec{k},\vec{k})M^{\mu'}_{m\sigma,n\sigma}(\vec{k},\vec{k})F^{sing}_{\mu,\mu'}(\delta\vec{k})\Big] + \\
& + \frac{1}{2}\sum_{mn,\sigma}^{occ}\int_{1BZ} d\vec{k}d\delta\vec{k}\sum_{\mu\mu'} M^{\mu}_{n\sigma,m\sigma}(\vec{k},\vec{k})M^{\mu'}_{m\sigma,n\sigma}(\vec{k},\vec{k})F^{sing}_{\mu,\mu'}(\delta\vec{k})
\end{aligned}
$$

First term calculated normally (summed). Second summed excluding zero. Last term analytically integrated.

For SPE-MP2:(Note them momentum conservation: $\vec{q} = \vec{k} - \delta\vec{k}$ and $\vec{q'} = \vec{k'} + \delta\vec{k}$) (The first term as an example)

$$\frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\int d\vec{k'}d\delta\vec{k}\frac{1}{\epsilon^{a\vec{q}\sigma,b\vec{q'}\sigma'}_{n\vec{k}\sigma,i\vec{k'}\sigma'}}\Big(\sum_{\mu\mu'} M^{\mu}_{n\vec{k}\sigma,a\vec{q}\sigma} M^{\mu'}_{i\vec{k'}\sigma',b\vec{q'}\sigma'} V^{non-sing}_{\mu,\mu'}(\delta\vec{k})\Big)^2$$

$$\frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\int d\vec{k'}d\delta\vec{k}\frac{1}{\epsilon^{a\vec{q}\sigma,b\vec{q'}\sigma'}_{n\vec{k}\sigma,i\vec{k'}\sigma'}}2\Big(\sum_{\mu\mu'} M^{\mu}_{n\vec{k}\sigma,a\vec{q}\sigma} M^{\mu'}_{i\vec{k'}\sigma',b\vec{q'}\sigma'} V^{non-sing}_{\mu,\mu'}(\delta\vec{k})\sum_{\mu\mu'} M^{\mu}_{n\vec{k}\sigma,a\vec{q}\sigma} M^{\mu'}_{i\vec{k'}\sigma',b\vec{q'}}$$

$$\Big[+\frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\int d\vec{k'}d\delta\vec{k}\frac{1}{\epsilon^{a\vec{q}\sigma,b\vec{q'}\sigma'}_{n\vec{k}\sigma,i\vec{k'}\sigma'}}\Big(\sum_{\mu\mu'} M^{\mu}_{n\vec{k}\sigma,a\vec{q}\sigma} M^{\mu'}_{i\vec{k'}\sigma',b\vec{q'}\sigma'} V^{sing}_{\mu,\mu'}(\delta\vec{k})\Big)^2 -$$

$$-\frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\int d\vec{k'}d\delta\vec{k}\frac{1}{\epsilon^{a\vec{k}\sigma,b\vec{k'}\sigma'}_{n\vec{k}\sigma,i\vec{k'}\sigma'}}\Big(\sum_{\mu\mu'} M^{\mu}_{n\vec{k}\sigma,a\vec{k}\sigma} M^{\mu'}_{i\vec{k'}\sigma',b\vec{k'}\sigma'} F^{sing}_{\mu,\mu'}(\delta\vec{k})\Big)^2\Big] +$$

$$+\frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\int d\vec{k'}d\delta\vec{k}\frac{1}{\epsilon^{a\vec{k}\sigma,b\vec{k'}\sigma'}_{n\vec{k}\sigma,i\vec{k'}\sigma'}}\Big(\sum_{\mu\mu'} M^{\mu}_{n\vec{k}\sigma,a\vec{k}\sigma} M^{\mu'}_{i\vec{k'}\sigma',b\vec{k'}\sigma'} F^{sing}_{\mu,\mu'}(\delta\vec{k})\Big)^2$$

First term calculated normally. Second term calculated skipping zero (the correction is just zero!). Same for third and forth term. Last term calculated analytically.