Total energy functionals

Patryk Kozlowski

May 30, 2024

We have the MO coefficients from a prior mean field calculation $C_{\mu p}$. I computed a form for a linearized GW density matrix in MO basis γ_{pq}. Now I want to alter the $C_{\mu p}$ to take into account this new density matrix. We can diagonalize the γ_{pq} to get the wave function rotations and orbital energies:

$$\boldsymbol{\gamma\psi} = \epsilon\boldsymbol{\psi} \tag{1}$$

Then we can get the new $C_{\mu p'}$ by:

$$C_{\mu p'} = \sum_p C_{\mu p}\psi_{pp'} \tag{2}$$

Then, I need to orthonormalize the new $C_{\mu p'}$ using the overlap matrix $S_{pp'}$ with

$$C_{\mu p} = C_{\mu p'}(S^{-1/2})_{pp'}C_{p'\nu} \tag{3}$$

Now that we have the density matrix at our disposition we want to use it to evaluate total energies. Any expression for the total energy will have the following form:

$$E_{\text{tot}} = T_s[?] + V_H[\gamma] + V_x[\gamma] + V_{\text{nuc, elec}}[\gamma] + V_{\text{nuc, nuc}} + E_{\text{corr}}[?] \tag{4}$$

where $V_H[\gamma]$ is the Hartree energy, $V_x[\gamma]$ is the exchange energy, $V_{\text{nuc, elec}}[\gamma]$ is the nuclear-electron attraction energy, and $V_{\text{nuc, nuc}}$ is the nuclear-nuclear repulsion energy. These terms remain constant to different total energy functions. T_s, which is defined as the kinetic energy, and E_{corr}, which is the correlation energy, are the terms that will change across different definitions of total energy functionals since either can contain a portion of correlation.

E_{corr} can either be evaluated using the Klein or Galitskii-Migdal formula. The Klein formula is given by:

$$E_{\text{corr}}^{\text{Klein}} = \frac{1}{2}\text{Tr}(\Omega^{\text{RPA}} - A^{\text{TDA}}) = \frac{1}{2}\text{Tr}(\Omega^{\text{RPA}}) - \frac{1}{2}\text{Tr}(A^{\text{TDA}}) \qquad (5)$$

where Ω^{RPA} are the RPA excitation energies and A^{TDA} is from the Tamm-Dancoff approximation. This is also known as the plasmon-pole form.

However, we know that the trace is invariant to unitary transformations and also cyclic permutations, so:

$$\text{Tr}(A^{\text{TDA}}) = \text{Tr}(A^{\text{TDA}}UU^{\dagger}) = \text{Tr}(U^{\dagger}A^{\text{TDA}}U) = \text{Tr}(\Omega^{\text{TDA}}) \qquad (6)$$

So with $E_{\text{corr}}^{\text{Klein}}$ we are quantifying the correlation energy by considering the difference between the RPA and TDA excitation energies for a given system. Since we found earlier that the TDA captures more correlation than the RPA, we can expect that $E_{\text{corr}}^{\text{Klein}}$ will be negative, or stabilizing, as we would expect.

$$E_{\text{c}}^{\text{GM}} = -\sum_{iam} \frac{M_{ia,m}^2}{\epsilon_a - \epsilon_i + \Omega_m} \qquad (7)$$

but this expression is given in terms of spin orbits, so after the integration we gain a factor of 2

$$E_{\text{c}}^{\text{GM}} = -2\sum_{iam} \frac{M_{ia,m}^2}{\epsilon_a - \epsilon_i + \Omega_m} \qquad (8)$$

where we have our transition densities:

$$M_{pq,u} = \sum_{ia} [pq|ia]X_{ia}^u \qquad (9)$$

where X_{ia}^u are the excitation vectors. After the spin integration, this simplified to:

$$M_{pq,u} = \sqrt{2}\sum_{ia} (pq|ia)X_{ia}^u \qquad (10)$$

We want to test 3 different total energy functionals:

$$E_{\text{tot}} = T_s[\gamma_0] + V_H[\gamma] + V_x[\gamma] + V_{\text{nuc, elec}}[\gamma] + V_{\text{nuc, nuc}} + E_{\text{corr}}^{\text{Klein}}[\gamma] \qquad (11)$$

$$E_{\text{tot}}^{GM} = T_s[\gamma_0] + V_H[\gamma_0] + V_x[\gamma_0] + V_{\text{nuc, elec}}[\gamma_0] + V_{\text{nuc, nuc}} + E_{\text{corr}}^{\text{GM}}[\gamma_0] \qquad (12)$$

$$E_{\text{tot}} = T_s[\gamma] + V_H[\gamma] + V_x[\gamma] + V_{\text{nuc, elec}}[\gamma] + V_{\text{nuc, nuc}} + E_{\text{corr}}^{\text{Klein}}[\gamma_0] \qquad (13)$$

Specifically, we will want to see the difference between 11 and 13. We are interested in formulating a table, which will corroborate vitals putin MOLGW, FHI-AIMS, and my implementation for the Galitskii-Migdal correlation energies. Then, I want to show how my energy for the Galitskii-Migdal deviates from that reported in the paper using HF, since mine uses the G_0W_0 density matrix that we investigated and the paper just uses the HF density matrix. Then I want to make a separate table, which compares the results of my Klein implemtation, for both of the interacting and noninteracting cases, with the responding result from PySCF. I will comment about how the discrepancy originates from the fact that the PySCF implementation uses and axillary bases, wail I didn't. Lastly, I want to make a table which documents the deviations between my Klein folly interacting and noninteracting cases cover for the total energies and the correlation energies. For the first table, I will just consider the two atoms Ne and He. For the second two tables, I will consider the water molecule, mating, and licl, to show more versatility.