

# Total energy functionals

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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  $\gamma_{pq}$ . Now I want to alter the  $C_{\mu p}$  to take into account this new density matrix. We can diagonalize the  $\gamma_{pq}$  to get the wave function rotations and orbital energies:

$$\gamma\psi = \epsilon\psi \quad (1)$$

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

$$C_{\mu p'} = \sum_p C_{\mu p} \psi_{pp'} \quad (2)$$

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

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

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:

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

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 functionals.  $T_s$ , which is defined as the kinetic energy, and  $E_{\text{corr}}$ , 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.

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

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

where  $\Omega^{\text{RPA}}$  are the RPA excitation energies and  $A^{\text{TDA}}$  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:

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

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.

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

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

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

where we have our transition densities:

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

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

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

We want to test 3 different total energy functionals:

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

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

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

I have been struggling a little bit with how to get The

$$T_s[\gamma_0] + V_{\text{nuc, elec}}[\gamma] \quad (14)$$

In my first line of code, I am generating the kinetic integrals in the AO basis:  $T_{\mu\nu}$ . Then, I rotate them into the MO basis using the noninteracting coefficients  $T_{pq} = \sum_{\mu\nu} C_{\mu p} T_{\mu\nu} C_{\nu q}$ . Finally, I get  $T_{\mu\nu}$  back from a rotation via  $\gamma^{GW} \rightarrow S_{\mu p}$  like  $T_{\mu\nu} = \sum_{pq} S_{\mu p} T_{pq} S_{\nu q}$ . But I am getting answers that are far off, so is this the right way to do it?

Specifically, we will want to see the difference between 11 and 12. 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.