

# Total energy functionals

Patryk Kozłowski

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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. The Galitskii-Migdal formula is given by:

$$E_{\text{corr}}^{\text{GM}} = -\frac{1}{2} \sum_{mia} \frac{M_{ai,m}^* M_{ai,m}}{\epsilon_a - \epsilon_i + \Omega_m - 2i\eta} - \frac{1}{2} \sum_{mai} \frac{M_{ia,m} M_{ia,m}^*}{\epsilon_a - \epsilon_i + \Omega_m + 2i\eta} \quad (7)$$

where we have our transition densities:

$$M_{pq,u} = \sum_{ia} (pq|ia) X_{ia}^u \quad (8)$$

where  $X_{ia}^u$  are the excitation vectors. In the restricted Hartree-Fock case, this simplified to:

$$M_{pq,u} = \sqrt{2} \sum_{ia} (pq|ia) X_{ia}^u \quad (9)$$

We want to test 3 different total energy functionals:

$$E_{\text{tot}} = T_s[\gamma_0] + V_H[\gamma] + V_x[\gamma] + V_{\text{nuc, elec}}[\gamma] + V_{\text{nuc, nuc}} + E_{\text{corr}}^{\text{Klein}}[\gamma] \quad (10)$$

$$E_{\text{tot}} = T_s[\gamma] + V_H[\gamma] + V_x[\gamma] + V_{\text{nuc, elec}}[\gamma] + V_{\text{nuc, nuc}} + E_{\text{corr}}^{\text{GM}}[G_0/\gamma_0] \quad (11)$$

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

Specifically, we will want to see the difference between 10 and 12.