Symmetry breaking in Green's function methods: the case of H_2

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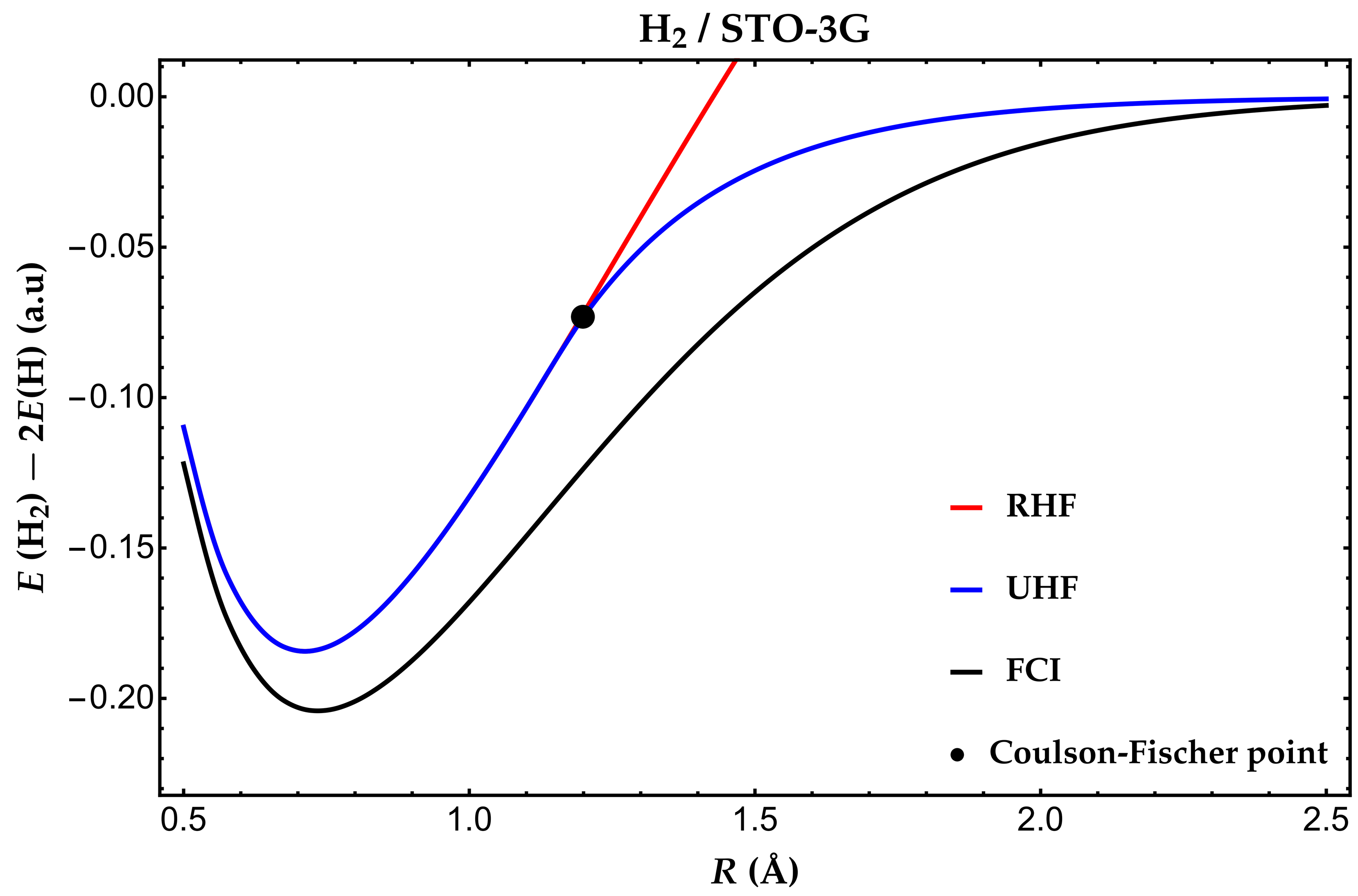
The dissociation problem



Green's function MBPT

The pillar of the Green's function MBPT is the time-ordered one-body Green's function

$$G(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) = \sum_i \frac{\phi_i(\boldsymbol{r}_1)\phi_i^*(\boldsymbol{r}_2)}{\omega - \varepsilon_i + i\eta} + \sum_a \frac{\phi_a(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_2)}{\omega - \varepsilon_a - i\eta} \tag{1}$$

which has poles at the charged excitations (i.e., ionization potentials and electron affinities) of the system. One can formulate the following eigenvalue equation

$$h(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_1) + \int d\boldsymbol{r}_2 \, \Sigma^{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2; \varepsilon_i)\phi_i(\boldsymbol{r}_2) = \varepsilon_i(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_1) \tag{2}$$

that resembles the Kohn-Sham equation but the self-energy is non local, energy-dependent and non Hermitian. Within the quasiparticle self-consistent (qs) scheme we update the one-electron quasiparticle energies and the orbitals until convergence is reached. These are obtained via the diagonalization of an effective Fock matrix, which includes explicitly a frequency-independent Hermitian self-energy defined as

$$\tilde{\Sigma}_{pq}^{xc} = \frac{1}{2}[\Sigma_{pq}^{xc}(\varepsilon_p) + \Sigma_{qp}^{xc}(\varepsilon_p)] \tag{3}$$

The Galitskii-Migdal correlation energy can be expressed as

$$E_c^{\text{GM}} = \int_0^{\infty} \frac{d\omega}{2\pi} \text{Tr}\{G(i\omega)\Sigma^c(i\omega)\} \tag{4}$$

GW approximation

In the so-called GW approximation the correlation part of the self-energy is given by

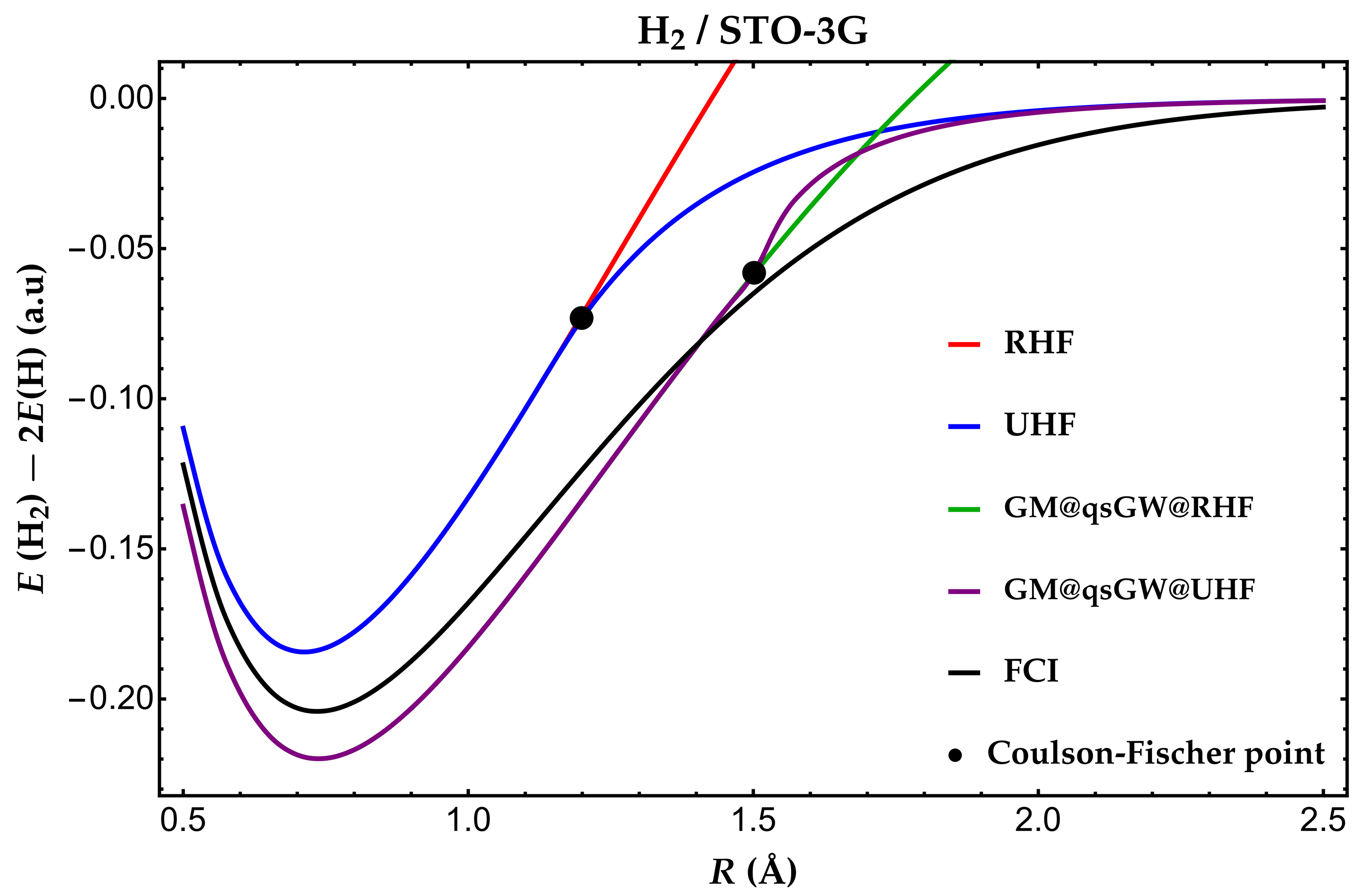
$$\Sigma_{pq}^{\text{GW}}(\omega) = \sum_{im} \frac{\langle pi|\chi_m^N\rangle \, \langle qi|\chi_m^N\rangle}{\omega - \varepsilon_i + \Omega^N} + \sum_{am} \frac{\langle pa|\chi_m^N\rangle \, \langle qa|\chi_m^N\rangle}{\omega - \varepsilon_a - \Omega^N} \tag{5}$$

where

$$\langle pq|\chi_m^N\rangle = \sum_{ia} \langle pi|qa\rangle \left(X_{m,ia}^N + Y_{m,ia}^N\right) \tag{6}$$

The correlation energy is given by the Galitskii-Migdal formula

$$E_c^{\text{GM}} = -\sum_{iam} \frac{\langle ia|\chi_m^N\rangle^2}{\varepsilon_a - \varepsilon_i + \Omega^N} \tag{7}$$



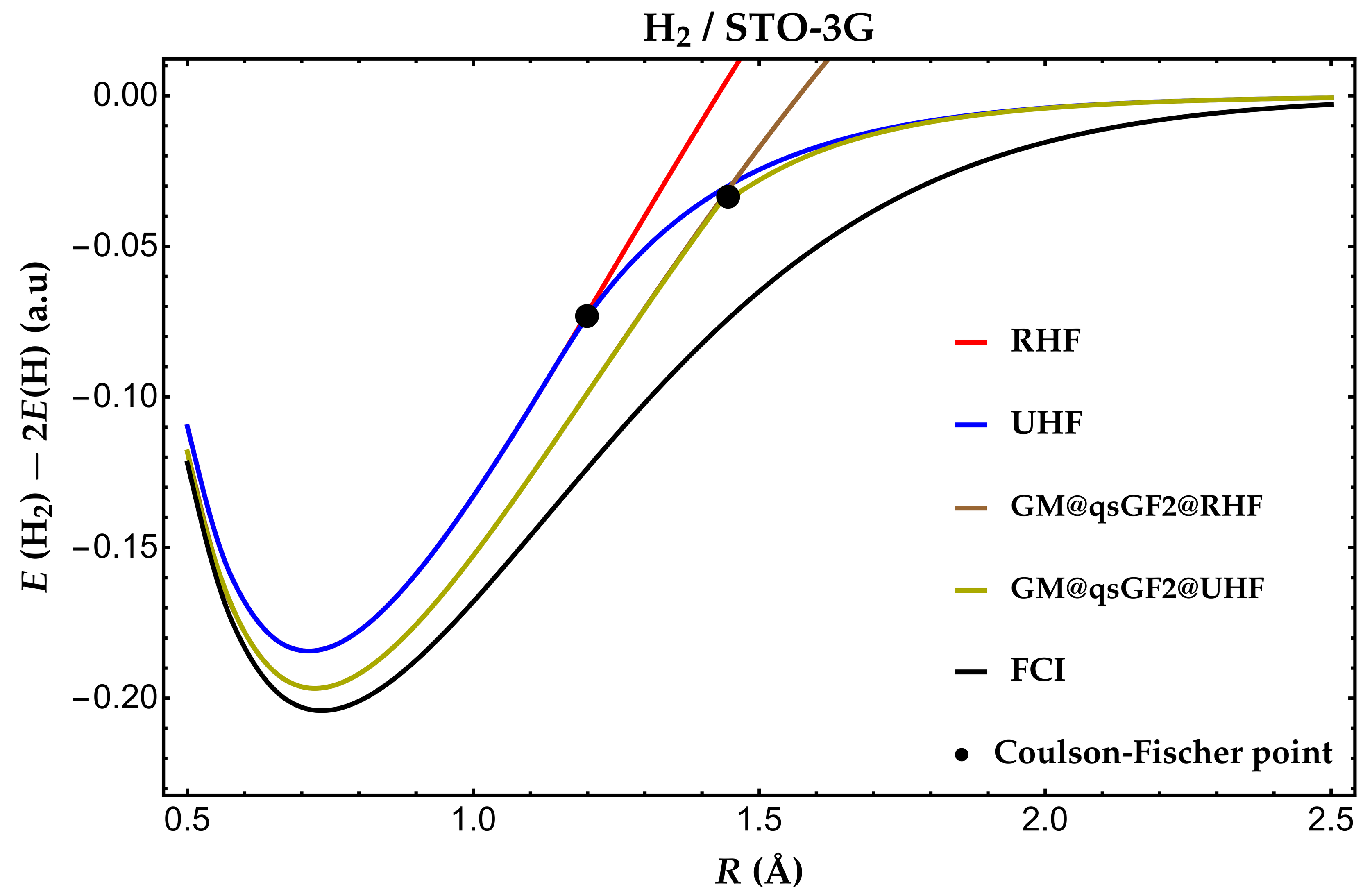
GF2 (or second-Born) approximation

In the GF2 approximation the correlation part of the self-energy is given by

$$\Sigma_{pq}^{\text{GF2}}(\omega) = \frac{1}{2}\sum_{iab} \frac{\langle iq||ab\rangle \, \langle ab||ip\rangle}{\omega + \varepsilon_i - \varepsilon_a - \varepsilon_b} + \frac{1}{2}\sum_{ija} \frac{\langle aq||ij\rangle \, \langle ij||ap\rangle}{\omega + \varepsilon_a - \varepsilon_i - \varepsilon_j} \tag{8}$$

The correlation energy is given by the MP2 correlation energy

$$E_c^{\text{MP2}} = -\frac{1}{4}\sum_{ijab} \frac{\langle ij||ab\rangle^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \tag{9}$$



GT (or T-matrix) approximation

The GT self-energy is

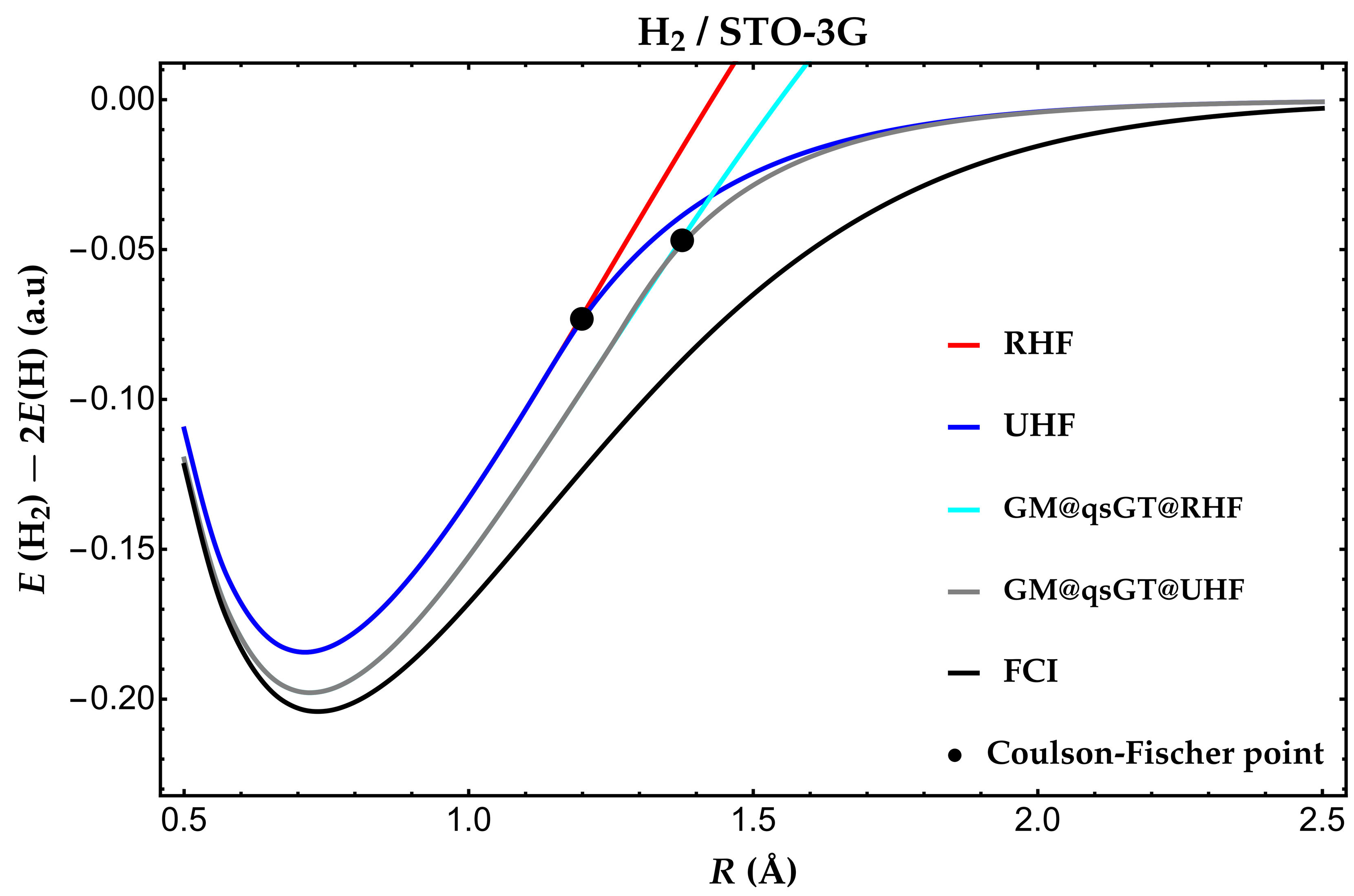
$$\Sigma_{pq}^{\text{GT}}(\omega) = \sum_{im} \frac{\langle pi|\chi_m^{N+2}\rangle \, \langle qi|\chi_m^{N+2}\rangle}{\omega + \varepsilon_i - \Omega_m^{N+2}} + \sum_{am} \frac{\langle pa|\chi_m^{N-2}\rangle \, \langle qa|\chi_m^{N-2}\rangle}{\omega + \varepsilon_a - \Omega_m^{N-2}} \tag{10}$$

where

$$\langle pi|\chi_m^{N\pm2}\rangle = \sum_{c<d} \langle pi||cd\rangle \, X_{m,cd}^{N\pm2} + \sum_{k<l} \langle pi||kl\rangle \, Y_{m,kl}^{N\pm2}, \tag{11}$$

The Galitskii-Migdal correlation energy is given by

$$E_c^{\text{GM}} = \sum_{ijm} \frac{\langle ij|\chi_m^{N+2}\rangle^2}{\varepsilon_i + \varepsilon_j - \Omega_m^{N+2}} - \sum_{abm} \frac{\langle ab|\chi_m^{N-2}\rangle^2}{\varepsilon_a + \varepsilon_b - \Omega_m^{N-2}} \tag{12}$$



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