Failure of the random phase approximation correlation energy

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Outline

- RPA for stretching simple molecules: success and failure
- The fractional occupation perspective: exact conditions for the energy
- Extension of many-body methods to fractional occupations
- Understanding strong correlation: the gap of the Hydrogen atom

RPA equations

The RPA ground-state correlation energy can be given by solving an excitation energy like problem

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \tag{1}$$

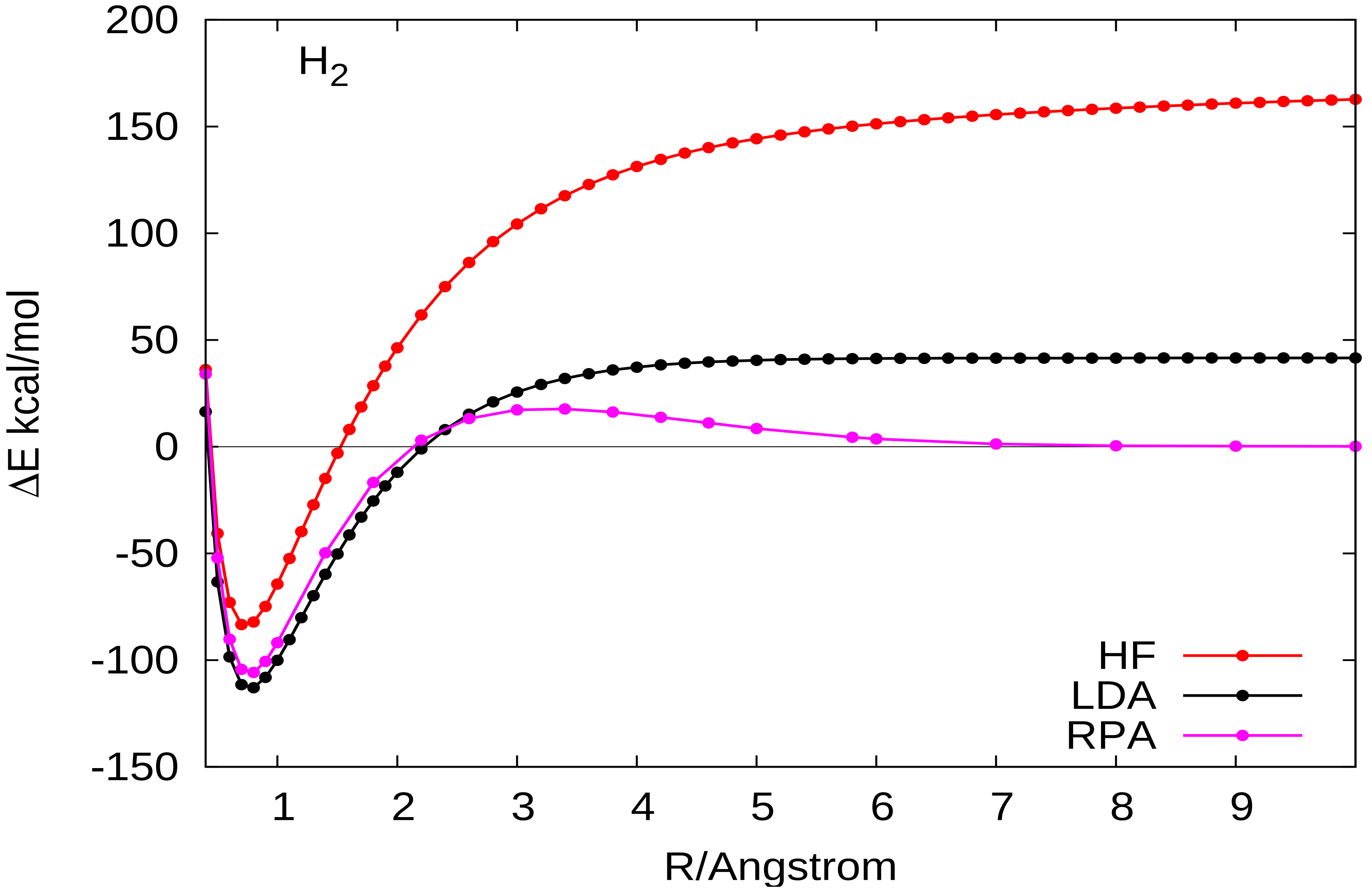
Direct RPA (RPA)

$$\begin{aligned} A_{ia,jb} &= (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle ib|aj\rangle \\ B_{ia,jb} &= \langle ij|ab\rangle \\ E_c^{\mathrm{RPA}} &= \frac{1}{2}\mathrm{Tr}(\omega - \mathbf{A}) \\ E_{\mathrm{RPA}} &= E_x^{\mathrm{EXX}} + E_c^{\mathrm{RPA}} \end{aligned}$$

Full RPA (RPAE)

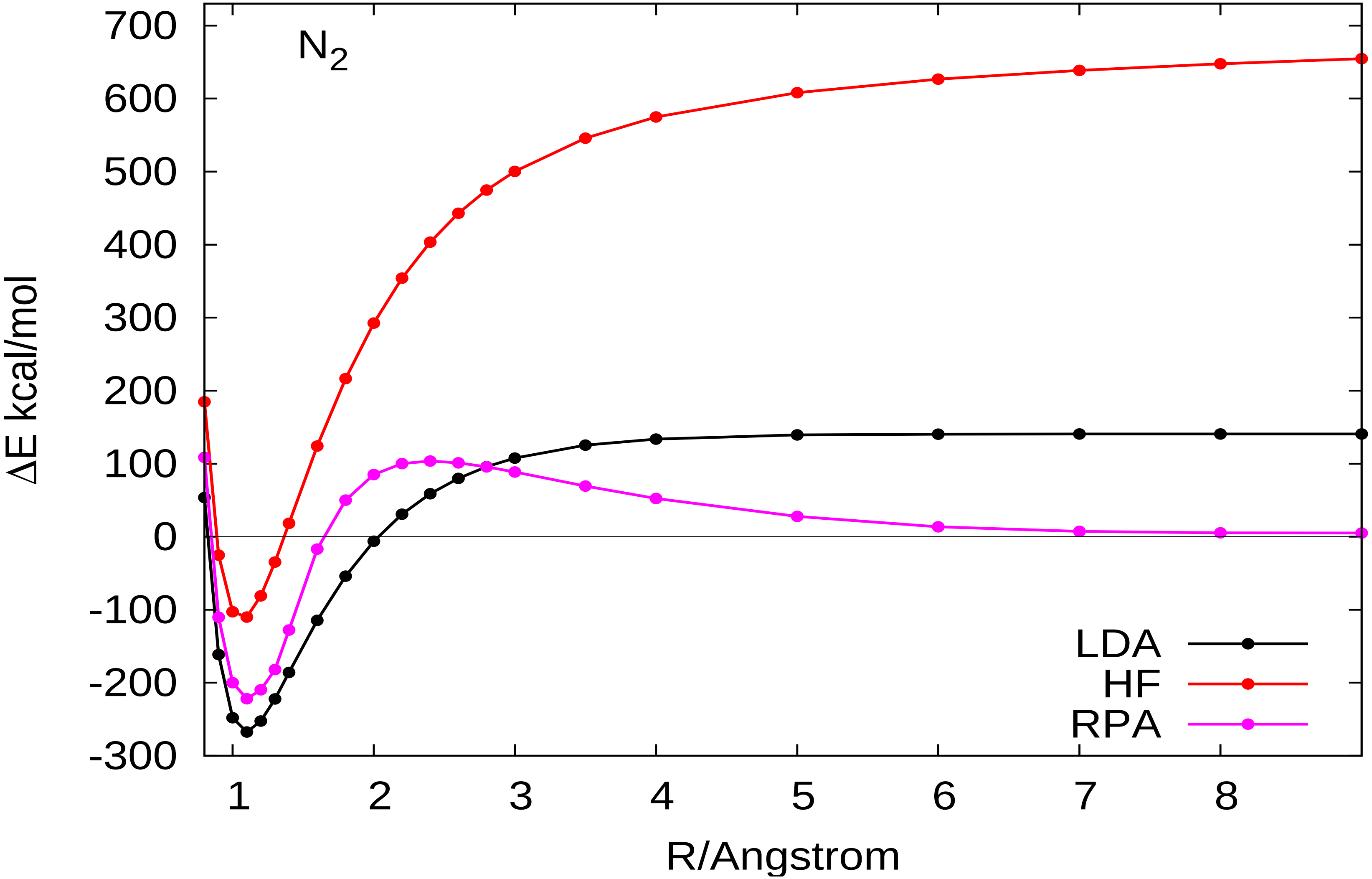
$$\begin{aligned} A_{ia,jb} &= (\epsilon_a^{\mathrm{HF}} - \epsilon_i^{\mathrm{HF}})\delta_{ia,jb} + \langle ib||aj\rangle \\ B_{ia,jb} &= \langle ij||ab\rangle \\ E_c^{\mathrm{RPAE}} &= \frac{1}{4}\mathrm{Tr}(\omega - \mathbf{A}) \\ E_{\mathrm{RPAE}} &= E_x^{\mathrm{HF}} + E_c^{\mathrm{RPAE}} \end{aligned}$$

H_2 binding curve



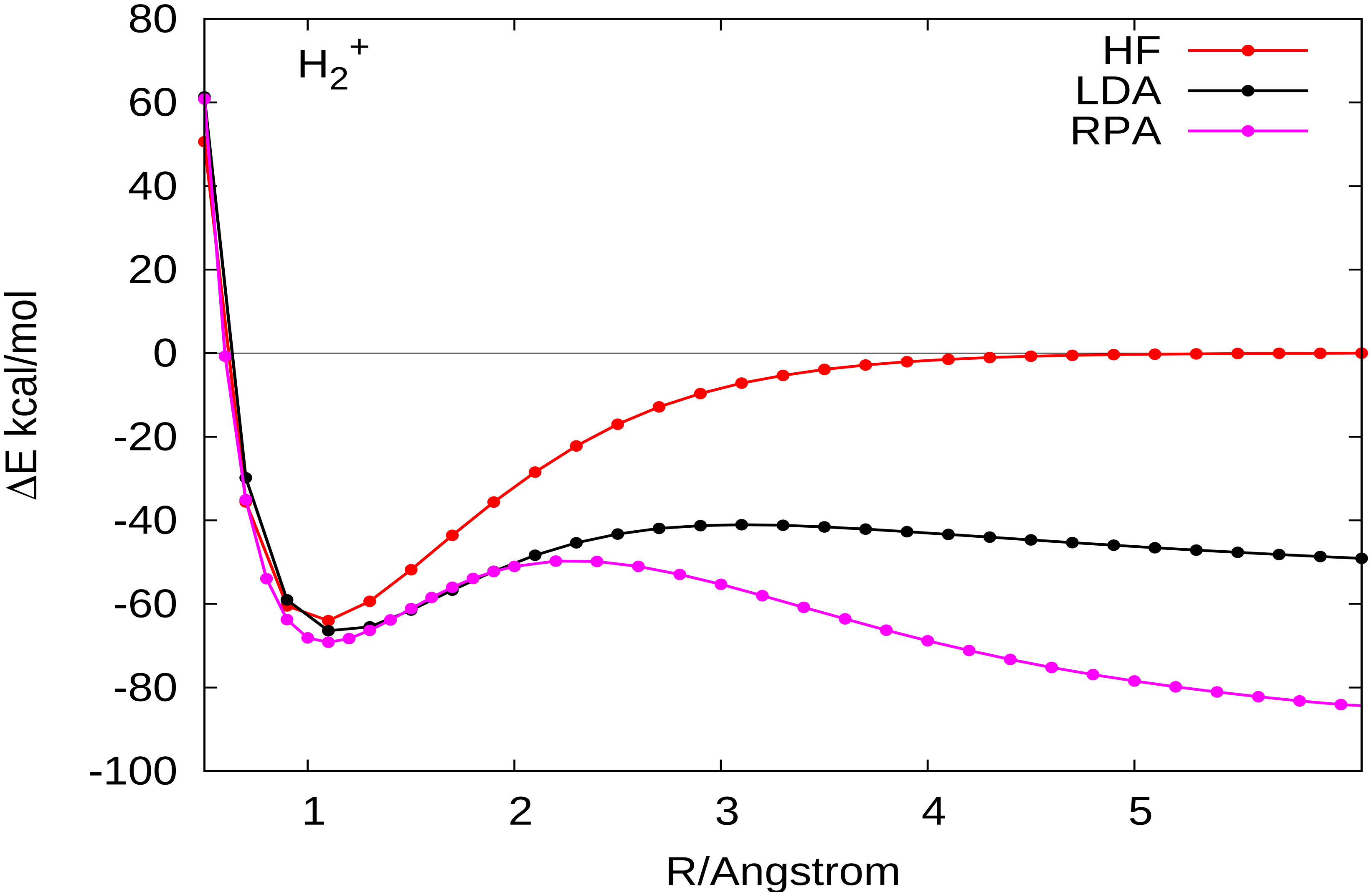
M. Fuchs, Y. M. Niquet, X. Gonze, and K. Burke, J. Chem. Phys. 122, 094116 (2005).

N_2 binding curve



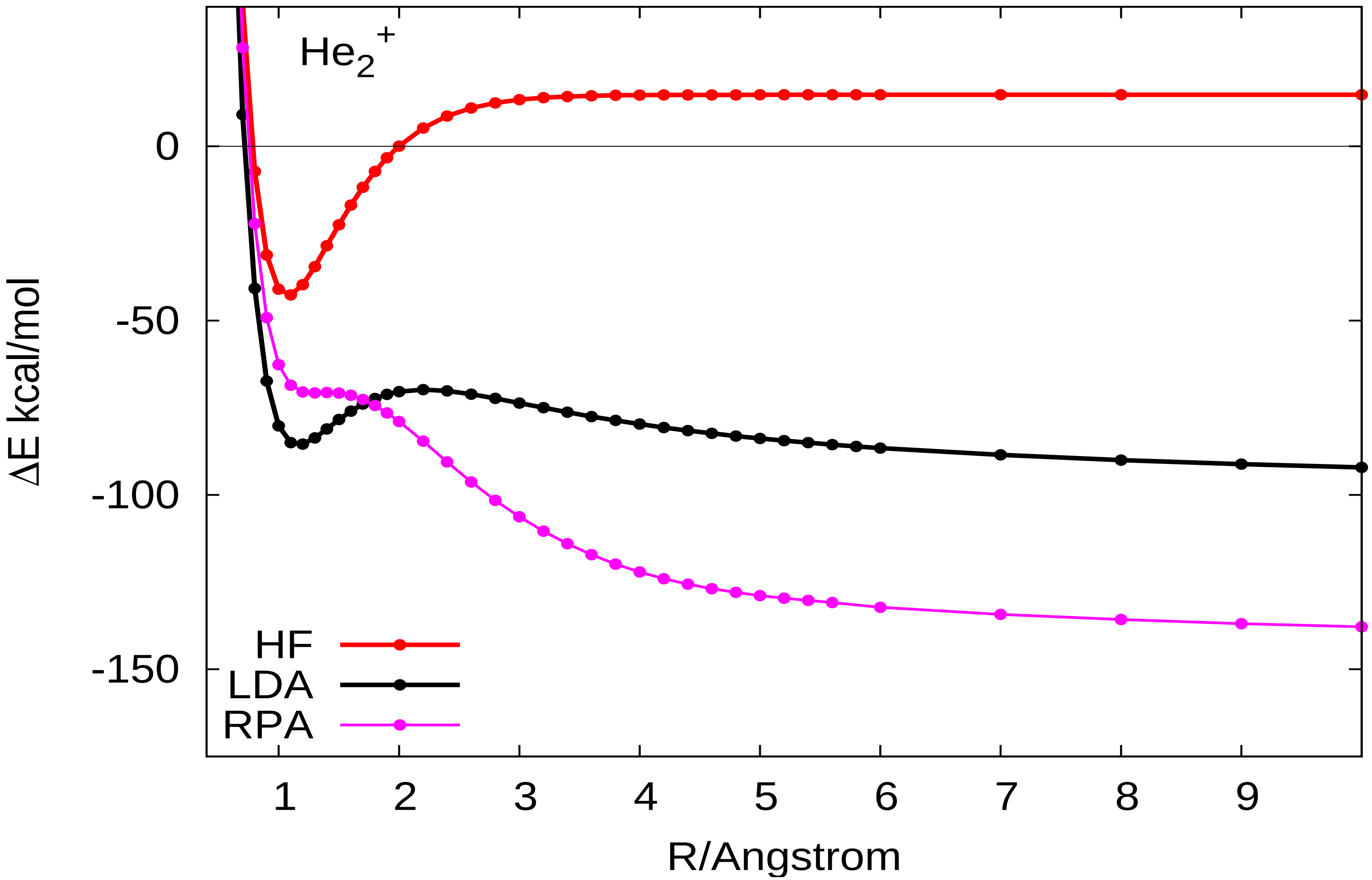
F. Furche, Phys. Rev. B 64 (2001)

H_2^+ binding curve



Mori-Sánchez, Cohen, Yang arXiv 0903.4403 (2009)

He_2^+ binding curve



Mori-Sánchez, Cohen, Yang arXiv 0903.4403 (2009)

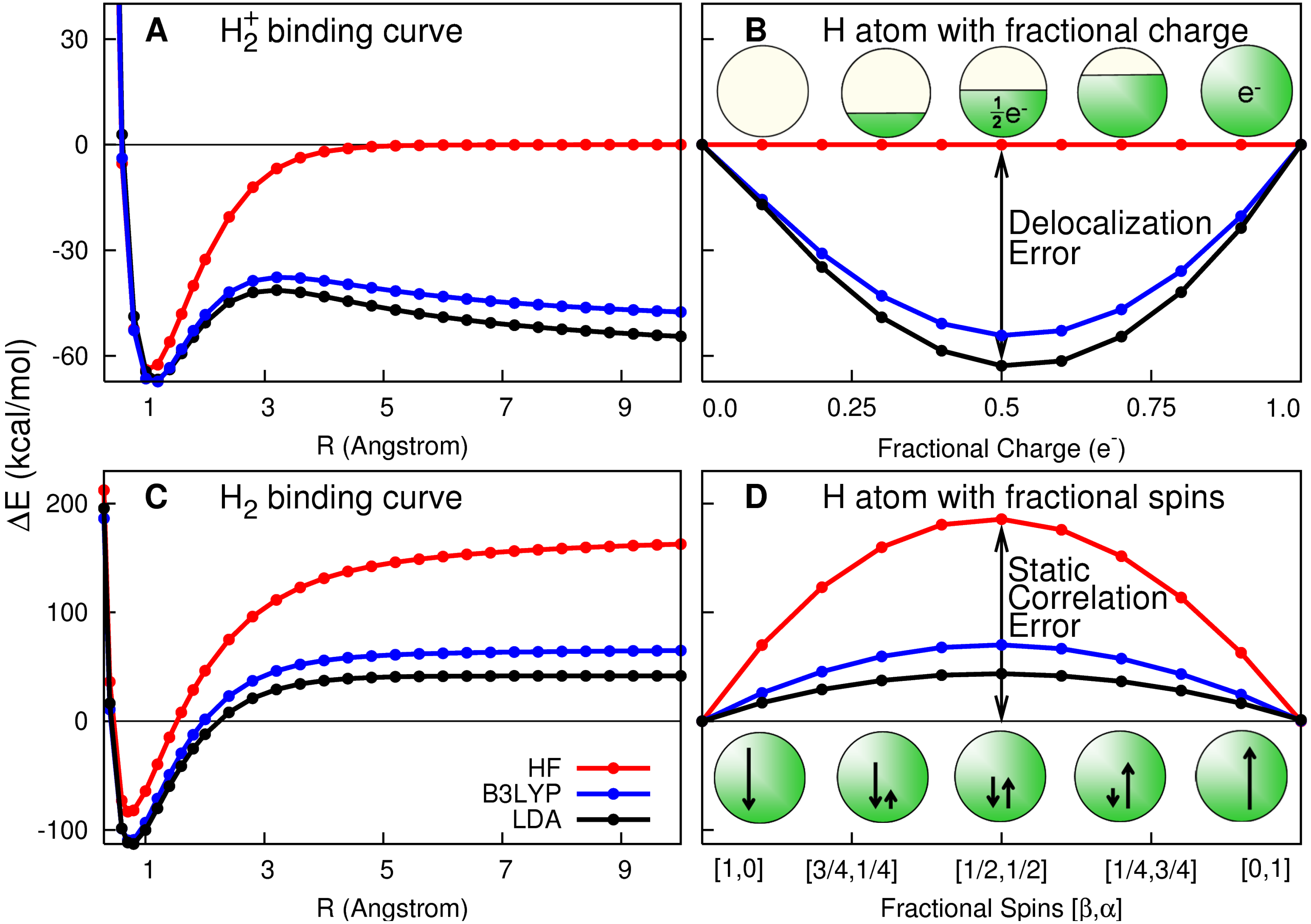
Understanding this behavior of RPA

There are successes of RPA that can be seen ranging from the correct description of the asymptotic limit of closed shell dissociation (e.g. H_2 and N_2), introduction of Van-der-Waals in weakly bound complexes. It can also perform reasonably well for the correlation energy of atoms and molecules at near equilibrium geometries. There are massive failures of dissocistion seen in odd electron sytems.

Can we understand the behaviour of the RPA correlation energy for the binding curves (in the infinitely stretched limit) of H_2 and H_2^+.

Let us first examine and understand the behaviour of some simple DFT methods.

The dissociation limit: the fractional occupation perspective



Cohen, Mori-Sánchez, Yang, Science 321 (2008)

Exact conditions for the exchange-correlation functional

- Fractional charges: linearity condition

$$E[N+\delta] = (1-\delta)E[N] + \delta E[N+1] \tag{2}$$

- Fractional spins: constancy condition

$$E[N_\alpha, N_\beta] = E[N-1+q, N-q] = E[N] \tag{3}$$

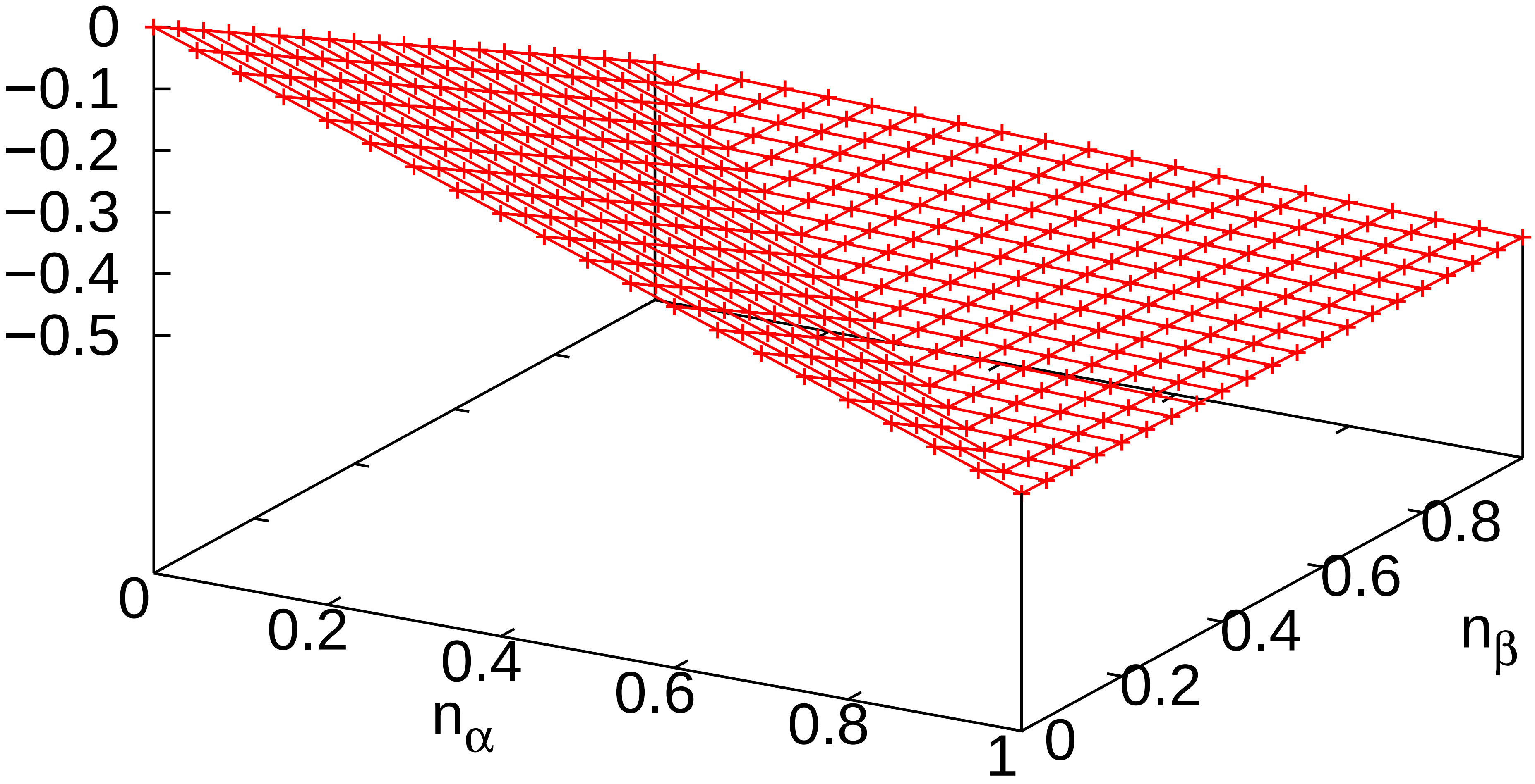
These two conditions are very important on their own but the true importance is not revealed until they are extended and unified to give a much more stringent condition:

- Fractional charges and spins combined: flat plane condition

$$E[N_\alpha + q\delta, N_\beta + (1-q)\delta] = (1-\delta)E[N] + \delta E[N+1] \tag{4}$$

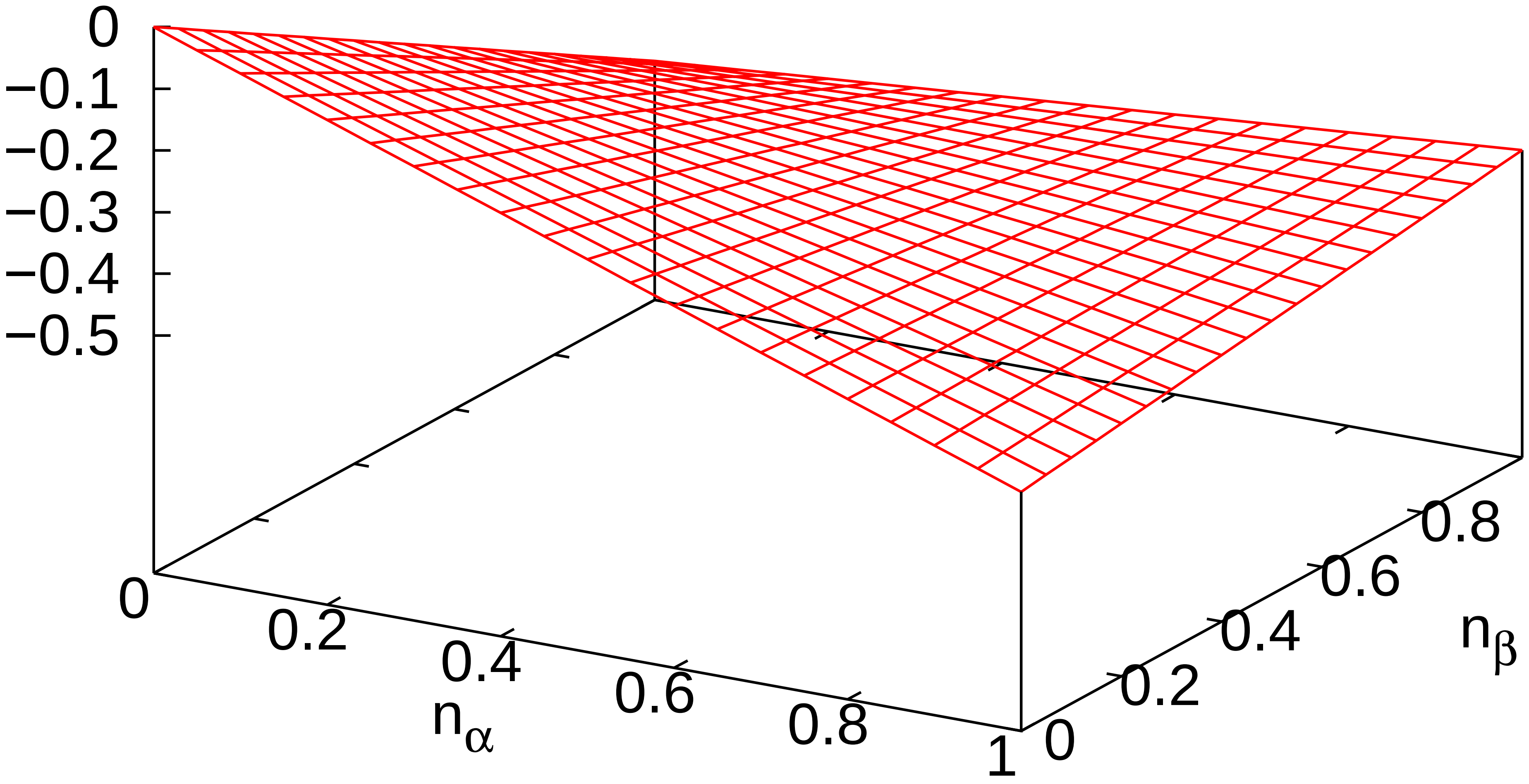
PPLB, PRL 49 (1982); Cohen, Mori-Sánchez, Yang, JCP 129(2008); Mori-Sánchez, Cohen, Yang, PRL 102(2009)

Exact energy of the hydrogen atom for fractional occupations



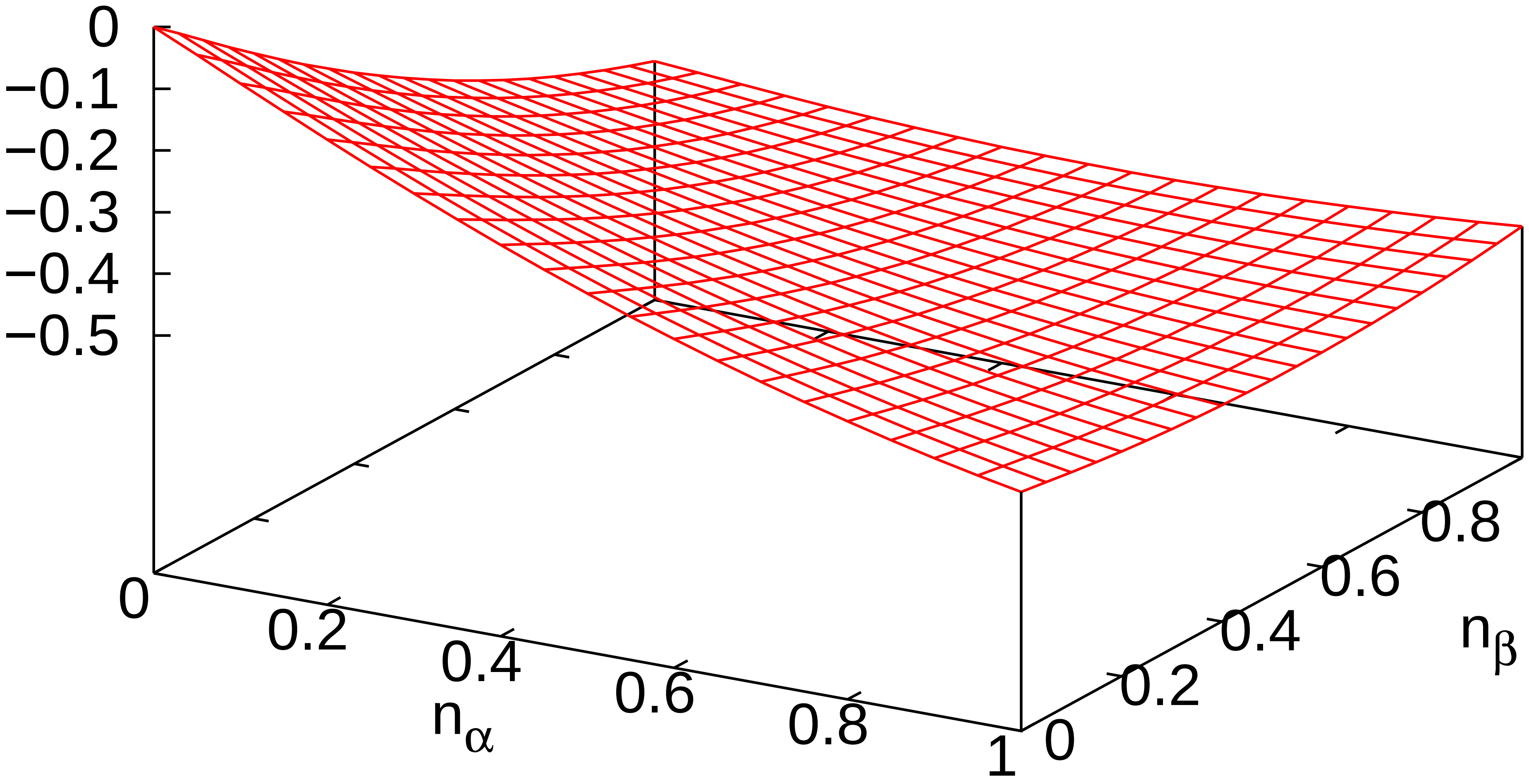
Mori-Sánchez, Cohen, Yang, PRL 102(2009)

Hartree-Fock



Mori-Sánchez, Cohen, Yang, PRL 102(2009)

BLYP



Errors of density functional approximations

There are many errors of density functionals that are encapsulated in the flat plane condition

$[\mathbf{0},\mathbf{0}] \rightarrow [\mathbf{0},\mathbf{1}]$	Self-interaction error or delocalization error
$[\mathbf{1},\mathbf{0}] \rightarrow [\mathbf{0},\mathbf{1}]$	Static correlation error (multideterminant problems)
$[\mathbf{0},\mathbf{0}] \rightarrow [(\frac{\mathbf{1}}{\mathbf{2}},\frac{\mathbf{1}}{\mathbf{2}})] \rightarrow [\mathbf{1},\mathbf{1}]$	Strongly correlated systems (gap of Mott insulators)

For example for the band-gap of strongly correlated systems, it is well known that smooth functionals of the density (e.g. LDA, GGA) will never be capable of giving a gap. This is also true for smooth functionals of the density matrix (e.g. orbital functionals, HF, EXX or screened exchange based functionals).

It is not clear whether the inclusion of eigenvalues and unoccupied orbitals to the functional, such as RPA, can provide discontiuous behavior that would help to describe strongly correlated systems.

We therefore extend RPA to fractional occupations and investigate its perfomance for the energy of the Hydrogen atom with 0 to 2 electrons.

Extension of DFT methods to fractional occupations

For methods where the energy can be expressed in terms of the one particle denisty matrix, (e.g. Kohn-Sham denisty functional or Hartree-Fock theory), $E[\rho_1]$

$$\rho_1^{N+\delta} = (1-\delta)\rho_1^N + \delta\rho_1^{N+1} \tag{5}$$

where

$$\rho_1^{N+\delta} = \sum_i n_i \phi_i(\mathbf{r})\phi_i(\mathbf{r}') \quad n_i = \begin{cases} 1, & \text{occupied} \\ \delta, & \text{frontier} \\ 0, & \text{virtual} \end{cases} \tag{6}$$

The fractional energy is given by

$$E^{\text{fractional}} \quad = \quad E[\rho_1^{N+\delta}] \tag{7}$$

note this can be (and is for approximate functionals) very different from

$$E^{\text{ensemble}} \quad = \quad (1-\delta)E[\rho_1^N] + \delta E[\rho_1^{N+1}] \tag{8}$$

Extension of Green's function methods to fractional occupations

For methods where the energy can be expressed in terms of the one particle Green's function (e.g. Hartree-Fock theory, MP2 or RPA), $E[G_0]$

$$G_0^{N+\delta}(i,j;E) = (1-\delta)G_0^N(i,j;E) + \delta G_0^{N+1}(i,j;E) \tag{9}$$

$$G_0^{N+\delta}(i,j;E) = \delta_{ij}\left\{\frac{(1-n_i)}{E-\epsilon_i+i\eta} - \frac{n_i}{E-\epsilon_i-i\eta}\right\} \tag{10}$$

$$\Pi_0^{N+\delta}(i,j,k,l;E) = \delta_{ik}\delta_{jl}\left\{\frac{(1-n_i)n_j}{E-(\epsilon_i-\epsilon_j)+i\eta} - \frac{n_i(1-n_j)}{E+(\epsilon_j-\epsilon_i)-i\eta}\right\} \tag{11}$$

This leads to a very simple change to the Green's function in terms of the occupation numbers, that each occupied orbital is transformed $\phi_i^2 \rightarrow n_i\phi_i^2$ and each unoccupied orbital is transformed $\phi_a^2 \rightarrow (1-n_a)\phi_a^2$

e.g. Casida, Phys. Rev. B 59 (1999)

MP2 energy expression including fractional occupations

$$E_c^{\mathrm{MP2}} = \frac{1}{4}\sum_{ij}^{\mathrm{all}}\sum_{ab}^{\mathrm{all}} n_i n_j \frac{\langle ij||ab\rangle^2}{\epsilon_i^{\mathrm{HF}} + \epsilon_j^{\mathrm{HF}} - \epsilon_a^{\mathrm{HF}} - \epsilon_b^{\mathrm{HF}}}(1-n_a)(1-n_b) \tag{12}$$

Interestingly we can now take the derivative of this expression with respect to occupation numbers, n_p, to give MP2 single particle energies (compare with second-order propogator theory)

$$\begin{aligned}\frac{\partial E_{\mathrm{MP2}}}{\partial n_p} &= \langle\phi_p| -\frac{1}{2}\nabla^2 + v_{ext}|\phi_p\rangle + \sum_i 2n_i\left(\langle ip|ip\rangle - \langle ip|pi\rangle\right) + \\ &\frac{1}{2}\left[\sum_{jab} n_j(1-n_a)(1-n_b)\frac{\langle pj||ab\rangle^2}{\epsilon_p+\epsilon_j-\epsilon_a-\epsilon_b} - \sum_{ijb} n_i n_j (1-n_b)\frac{\langle ij||pb\rangle^2}{\epsilon_i+\epsilon_j-\epsilon_p-\epsilon_b}\right]\end{aligned}$$

Cohen, Mori-Sánchez, Yang JCTC, 5 (2009)

RPA equations for fractional occupations

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \tag{13}$$

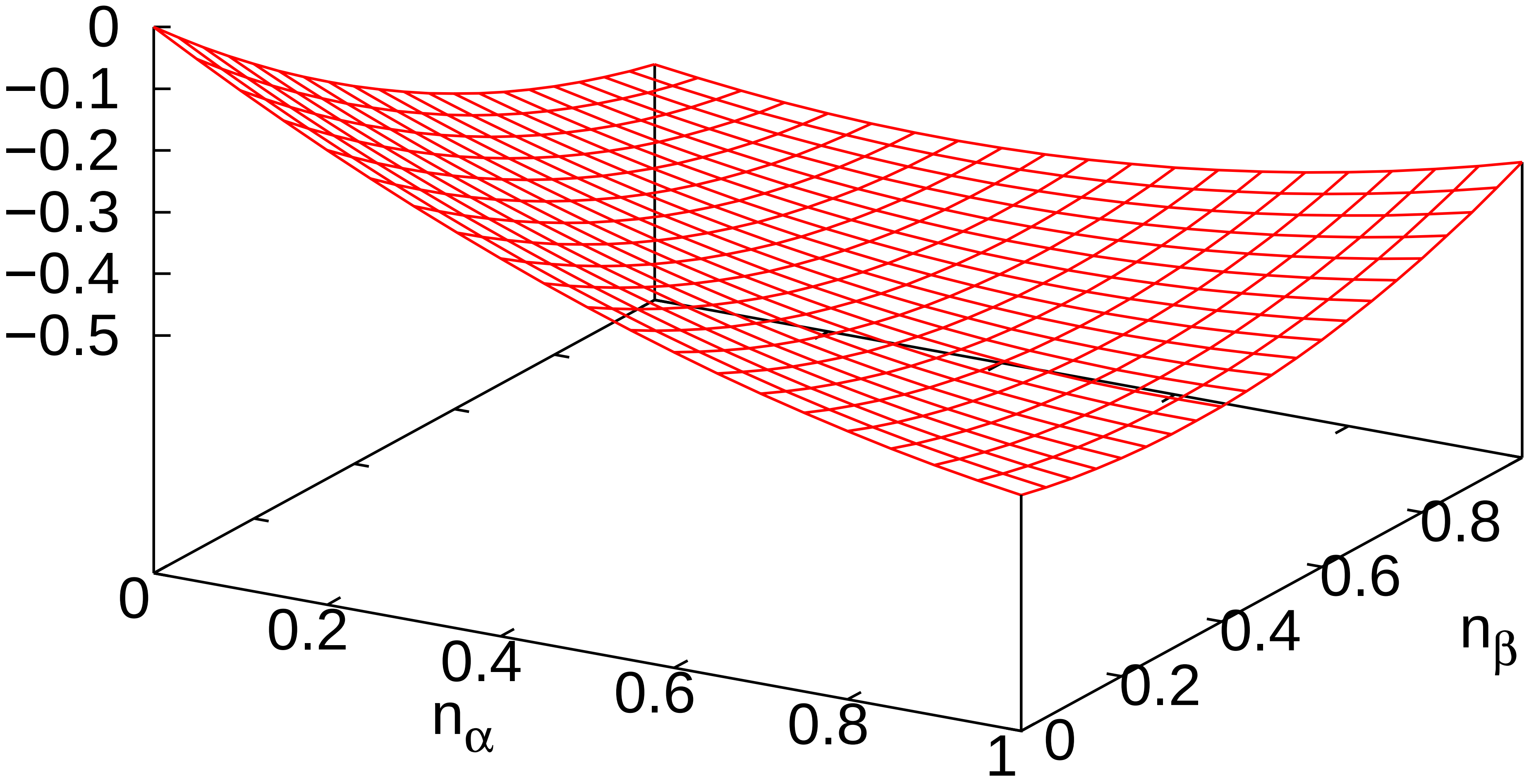
$$\begin{aligned} A_{ia,jb} &= (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle ib|aj\rangle \sqrt{n_i n_j (1-n_a)(1-n_b)} \\ B_{ia,jb} &= \langle ij|ab\rangle \sqrt{n_i n_j (1-n_a)(1-n_b)} \end{aligned} \tag{14}$$

In this case the **A** and **B** matrices are of size $(n_{\text{occ}} + n_{\text{frac}})(n_{\text{virt}} + n_{\text{frac}})$. Note that this is very different to the expressions from the ensemble of the energy (or the propogator Π_0)

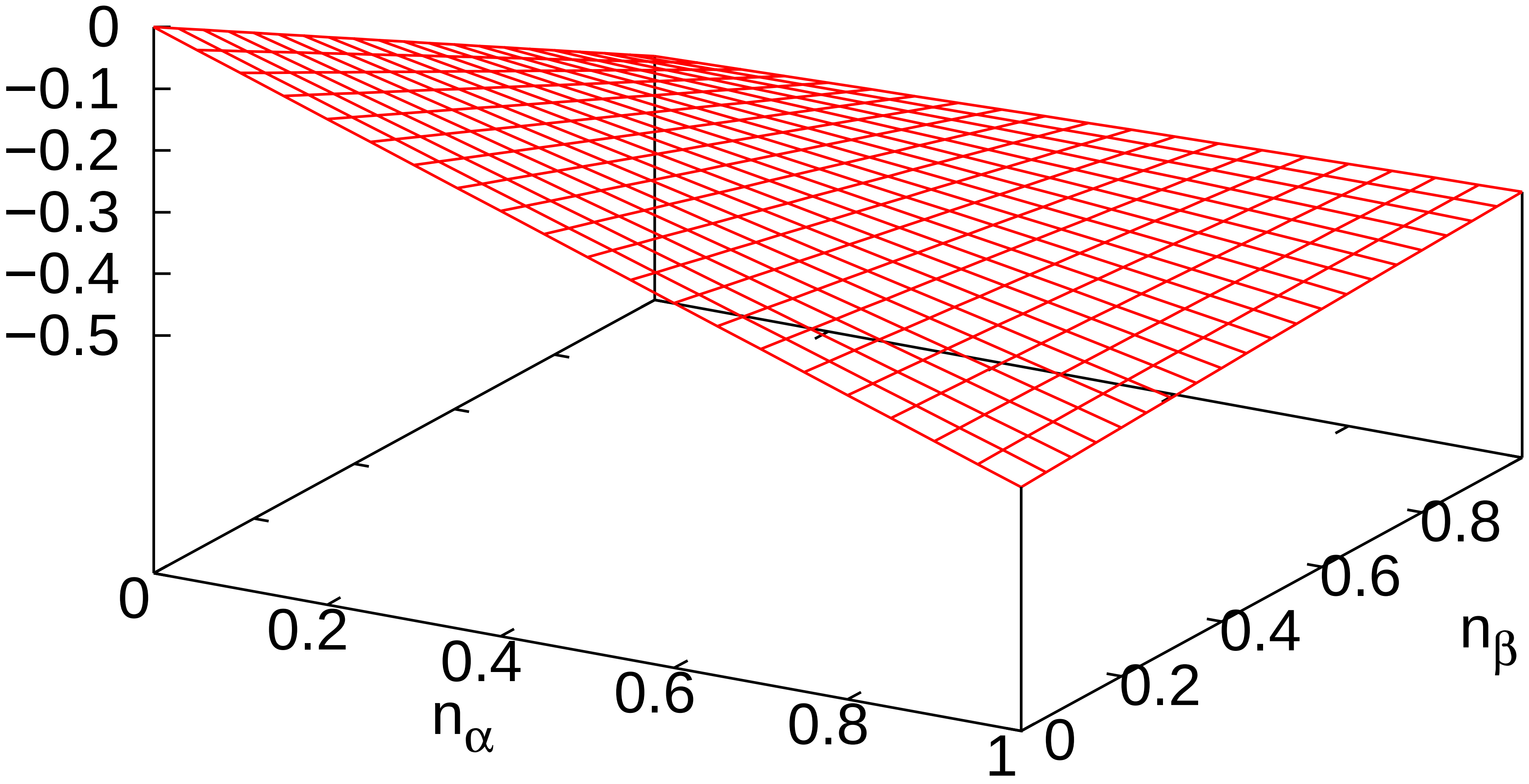
$$\begin{aligned} A_{ia,jb} &= (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle ib|aj\rangle (n_i - n_a)(n_j - n_b) \\ B_{ia,jb} &= \langle ij|ab\rangle (n_i - n_a)(n_j - n_b) \end{aligned} \tag{15}$$

Note only Eq. (14) corresponds to the RPA dissociation limits of molecules.

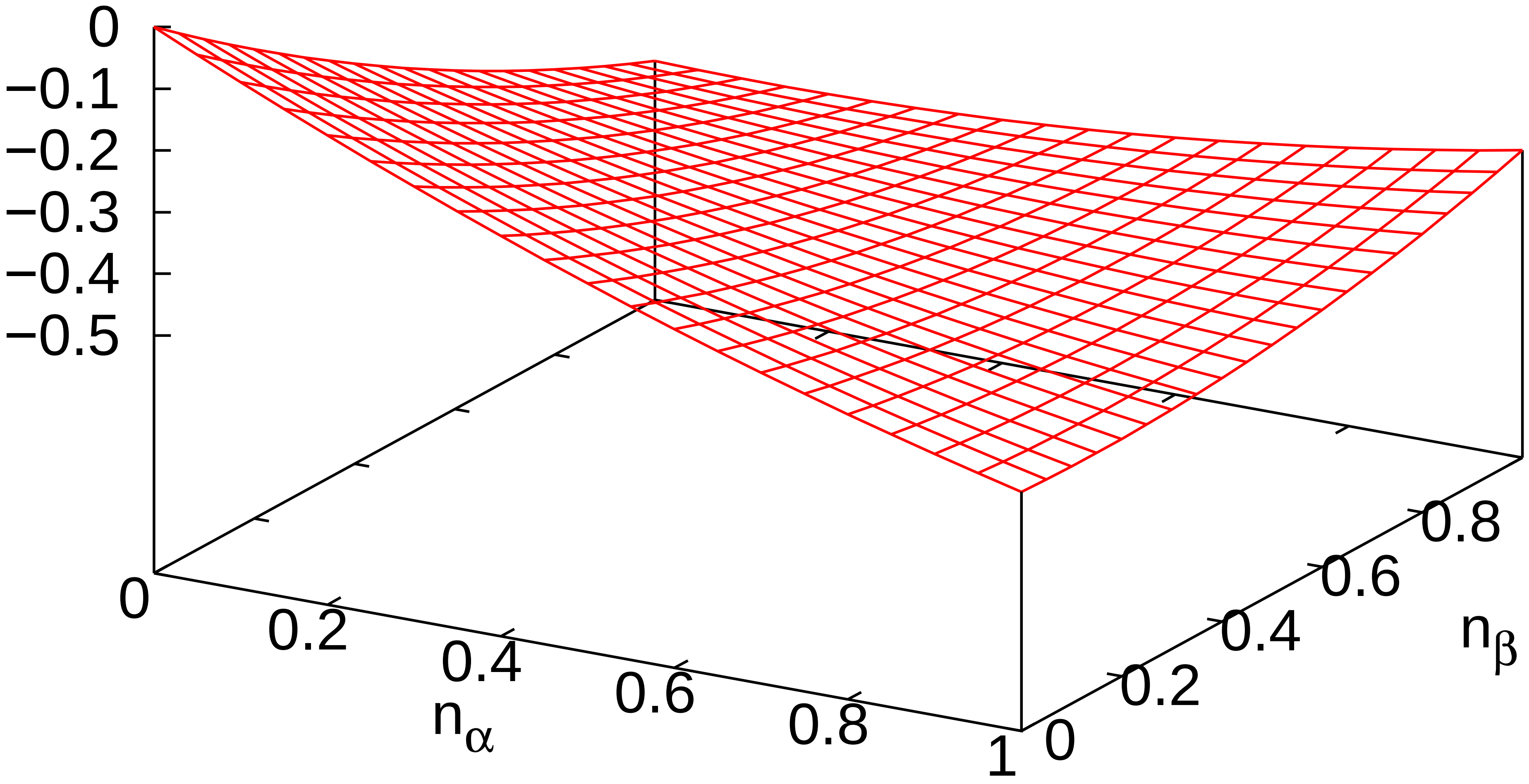
RPA



RPAE

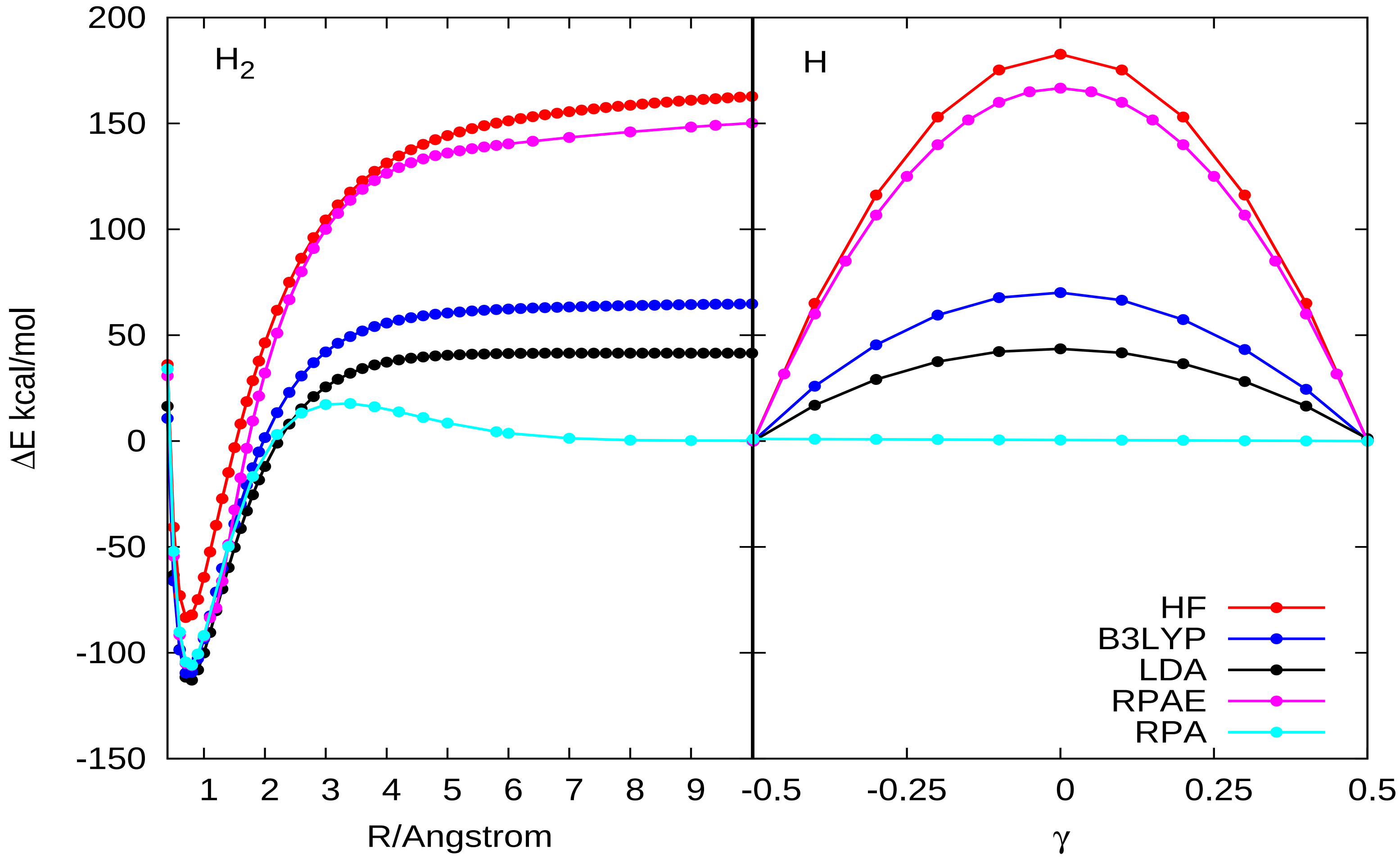


RPA range-separated

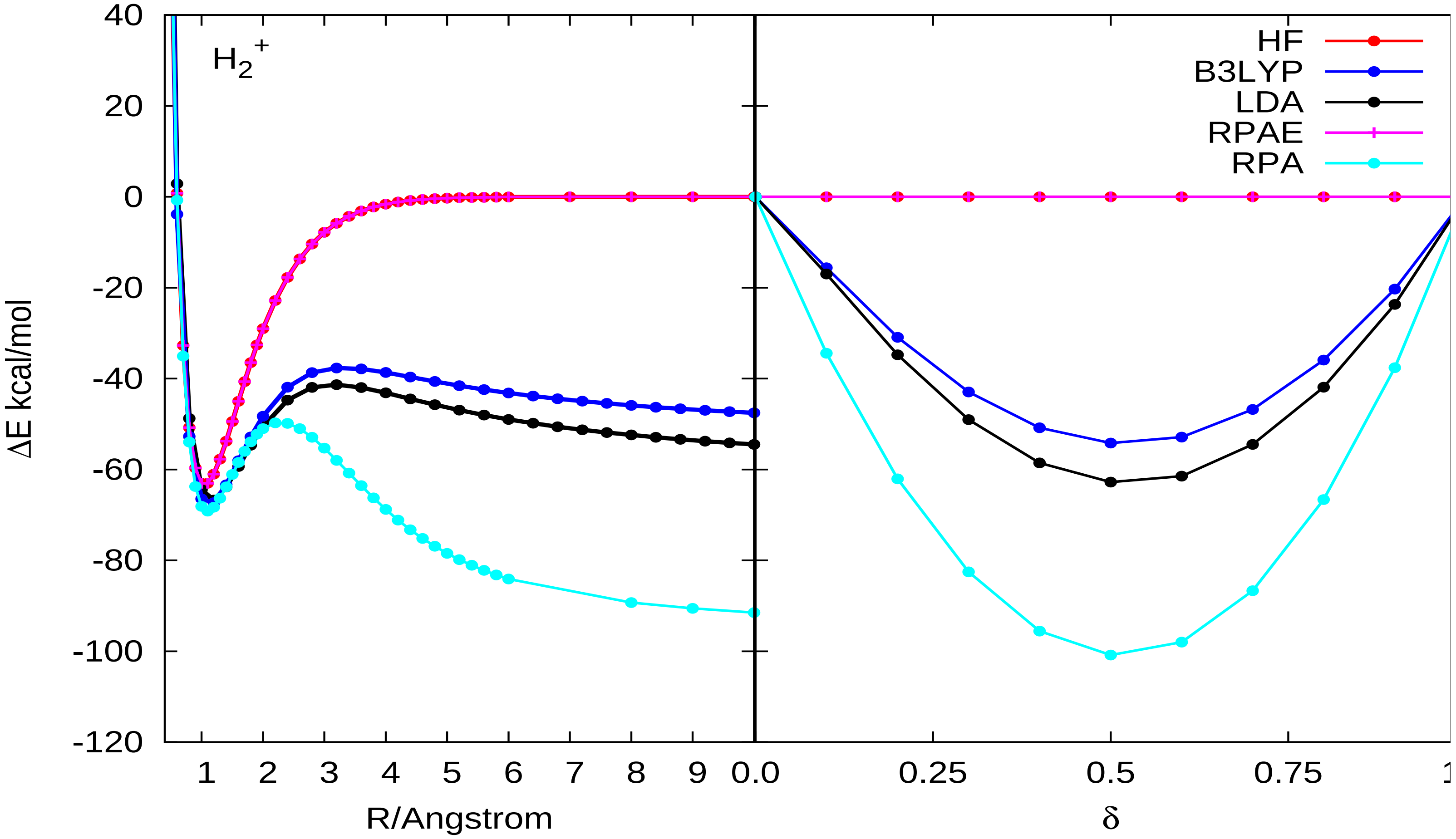


e.g. J. Toulouse *et al*, Phys. Rev. Lett. 102, 096404 (2009) and B. G. Janesko *et al* , J. Chem. Phys. 130, 081105 (2009).

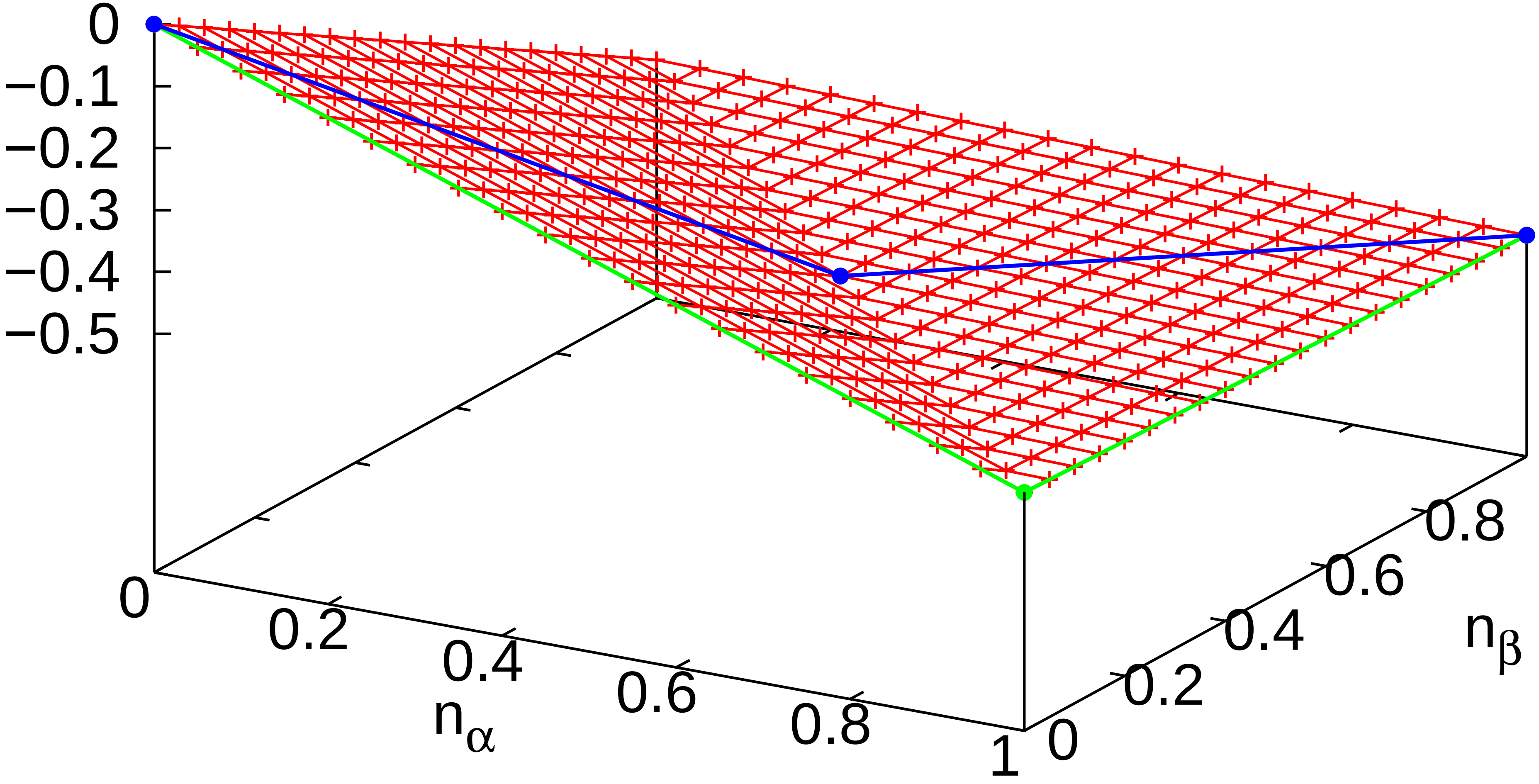
H_2 compared with the fractional spin H atom



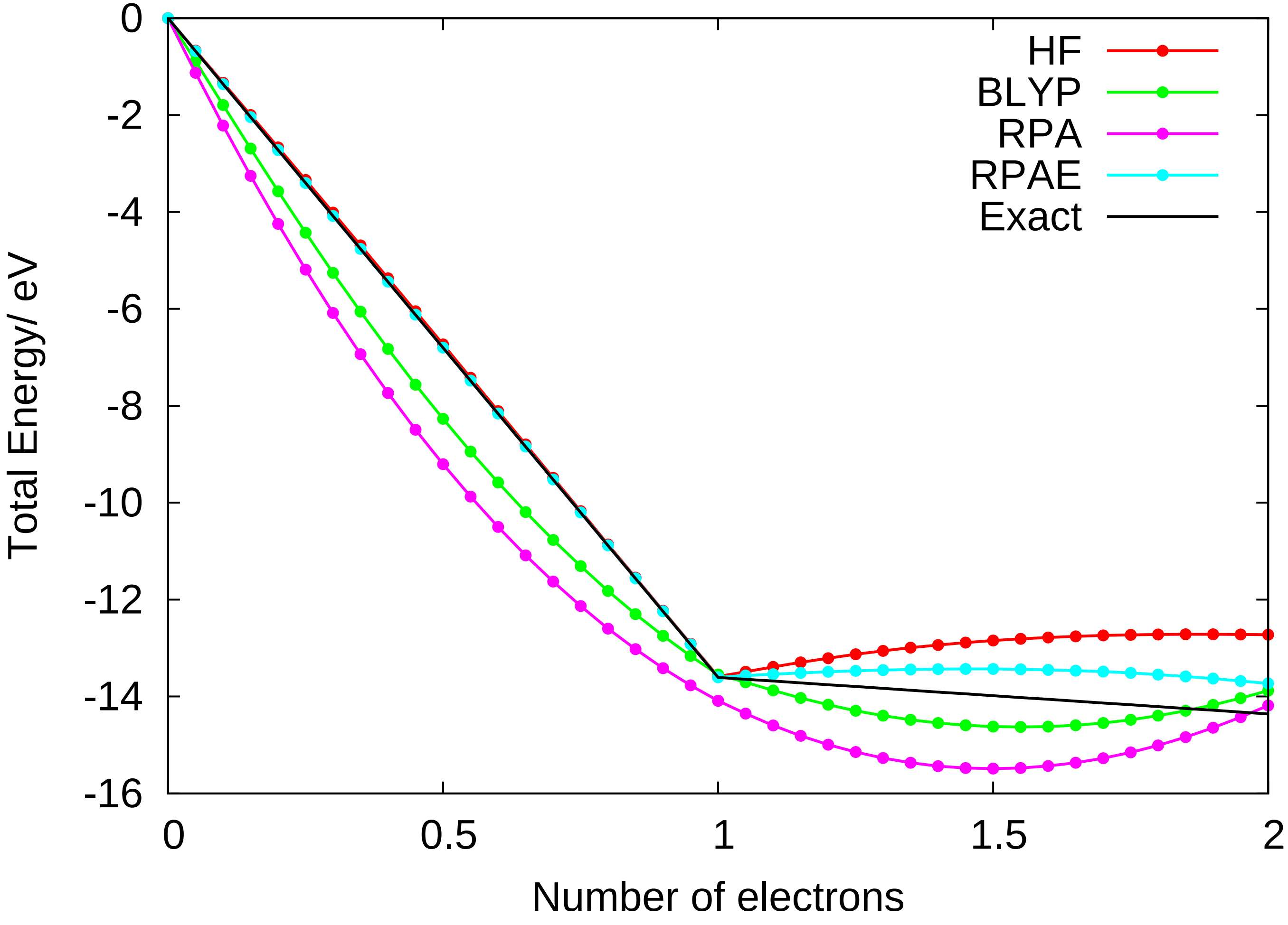
H_2^+ compared with the fractionally charged H atom



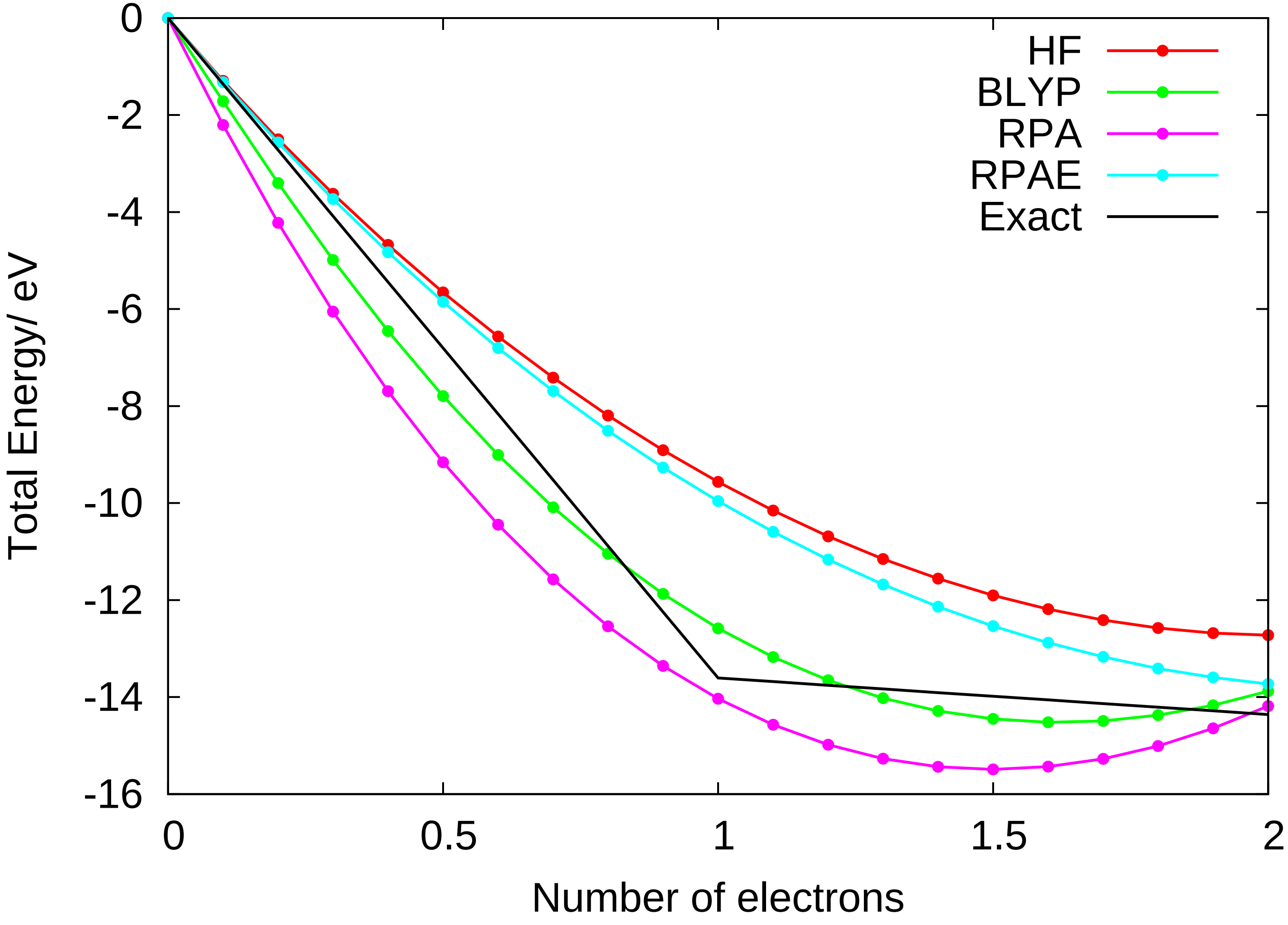
Hydrogen atom: a challenge for electronic structure methods



The band gap problem in DFT: $[\mathbf{0},\mathbf{0}] \rightarrow [\mathbf{1},\mathbf{0}] \rightarrow [\mathbf{1},\mathbf{1}]$



The gap of a Mott insulator $[\mathbf{0},\mathbf{0}] \rightarrow [(\mathbf{\frac{1}{2}},\mathbf{\frac{1}{2}})] \rightarrow [\mathbf{1},\mathbf{1}]$



Conclusions

- The flat plane condition for the energy is a very stringent test for electronic structure methods

  Can a method work for both the stretching of H_2 and H_2^+ (and their gaps)?

- RPA methods do not simply overcome these dissociation problems also seen in simpler DFT energy expressions, despite the increase in complexity.
- The derivatives $\frac{\partial E^{\mathrm{RPA}}}{\partial n_i}$ can also be evaluated
- Discontinuous energy expressions are needed to treat even a system as simple as the Hydrogen atom.