

Notes on Basis Correction

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I'll present the ideas and equations at play to derive a DFT method to correct for the basis set incompleteness of wavefunction calculations. Everything comes from the work of Giner *et al.*, and the two good papers to read about this are:

- “Curing basis-set convergence of wave-function theory using density functional theory: A systematically improvable approach”
E. Giner, B. Pradines, A. Ferte, R. Assaraf, A. Savin, J. Toulouse
[10.1063/1.5052714](https://doi.org/10.1063/1.5052714)
- “A Density-Based Basis-Set Correction For Wave Function Theory”
P.-F. Loos, B. Pradines, A. Scemama, J. Toulouse, E. Giner
[10.1021/acs.jpcclett.9b01176](https://doi.org/10.1021/acs.jpcclett.9b01176)

A reader interested in implementing this can go straight to Section 4, and a talk more centered on links to range-separation can be found [here](#).

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1 Fundamental idea

The idea is to derive a DFT functional $E^{\mathcal{B}}[n]$ able to capture the out-of-basis set effects that are absent from an energy $E_{\text{wft}}^{\mathcal{B}}$ calculated at any wavefunction

level in a basis set \mathcal{B} :

$$E = E_{\text{wft}}^{\mathcal{B}} + E^{\mathcal{B}}[n]. \quad (1)$$

We will discover that $E^{\mathcal{B}}[n]$ must recover the physics of short-range correlation. Indeed, what is typically difficult to describe in any wavefunction method is the cusp found at electron-electron coalescence in two-body objects (the wavefunction, the pair-density, the Coulomb interaction itself, \dots). Consider in Figure 1 the exact wavefunction compared to the FCI wavefunctions, exact *within a basis*: the difficulty within a basis to describe the system at short electron-electron range is a cause of error even in the case of FCI calculations.

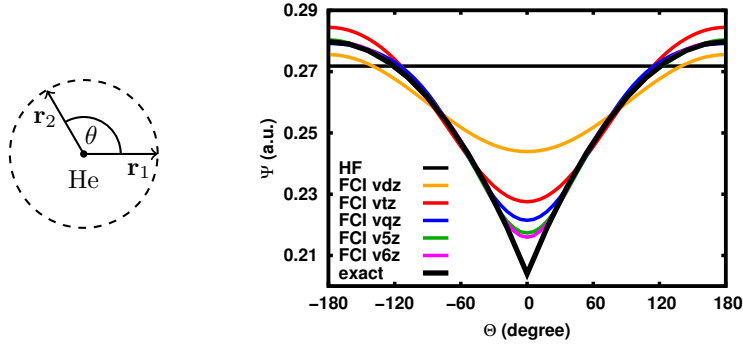


Figure 1: Exact wavefunctions of the Helium atom at the electron coordinates $\mathbf{r}_1 = (0.5, 0., 0.)$ bohr and $\mathbf{r}_2 = (0.5 \cos \theta, 0.5 \sin \theta, 0.)$ bohr, with Dunning basis sets ranging from cc-pVDZ to cc-pV6Z (abbreviated as vXz) and shown as a function of the relative angle θ . Are provided for reference: the Hartree-Fock wavefunction and an exact wavefunction calculated with a highly accurate 418-term Hylleraas-type wavefunction. Notice that a correct behavior at long electron-electron range is fairly easy to obtain, while reproducing the short range behavior is challenging for any finite basis set.

2 Coulomb interaction projected in a basis

Coulomb interaction

We will compare the true Coulomb interaction with the effective Coulomb interaction expressed in a basis. Let's first look at the Coulomb interaction operator made from the Coulomb interaction $w(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4})$:

$$\hat{W}_{\text{ee}} = \int_{\mathbf{1}\mathbf{2}\mathbf{3}\mathbf{4}} \hat{\Psi}^\dagger(\mathbf{4}) \hat{\Psi}^\dagger(\mathbf{3}) \underbrace{\left(\frac{1}{r_{12}} \delta_{14} \delta_{23} \right)}_{w(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4})} \hat{\Psi}(\mathbf{2}) \hat{\Psi}(\mathbf{1}), \quad (2)$$

and at it's expectation value on a wavefunction $\Psi^{\mathcal{B}}$:

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle = \int_{\mathbf{12}} \frac{1}{r_{\mathbf{12}}} n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}), \quad (3)$$

with the pair density defined as $n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}) \equiv n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{2}, \mathbf{1})$ with:

$$n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) = \langle \Psi^{\mathcal{B}} | \hat{\Psi}^\dagger(\mathbf{4}) \hat{\Psi}^\dagger(\mathbf{3}) \hat{\Psi}(\mathbf{2}) \hat{\Psi}(\mathbf{1}) | \Psi^{\mathcal{B}} \rangle. \quad (4)$$

In the following, we will go back and forth from second quantization operators to real space field operators, as follows:

$$\hat{a}_p = \int_{\mathbf{1}} \phi_p(\mathbf{1}) \hat{\Psi}(\mathbf{1}) \quad \text{and} \quad \hat{\Psi}(\mathbf{1}) = \sum_p \phi_p(\mathbf{1}) \hat{a}_p, \quad (5)$$

and for example the pair density above can hence be re-written with the reduced-density matrix $\Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}] = \langle \Psi^{\mathcal{B}} | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_n \hat{a}_m | \Psi^{\mathcal{B}} \rangle$ as:

$$n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) = \sum_{mnpq} \Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}] \phi_p(\mathbf{4}) \phi_q(\mathbf{3}) \phi_n(\mathbf{2}) \phi_m(\mathbf{1}). \quad (6)$$

Effective interaction

We aim at deriving the corresponding objects expressed within a basis. Starting from the Coulomb operator in second quantization:

$$\hat{W}_{\text{ee}}^{\mathcal{B}} = \sum_{rstu \in \mathcal{B}} V_{rs}^{tu} \hat{a}_t^\dagger \hat{a}_u^\dagger \hat{a}_s \hat{a}_r, \quad (7)$$

we are able to define an effective interaction $w^{\mathcal{B}}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4})$ within the basis by converting the second quantization operators to real space field operators:

$$\hat{W}_{\text{ee}}^{\mathcal{B}} = \int_{\mathbf{1234}} \hat{\Psi}^\dagger(\mathbf{4}) \hat{\Psi}^\dagger(\mathbf{3}) \underbrace{\left(\sum_{rstu} V_{rs}^{tu} \phi_t(\mathbf{4}) \phi_u(\mathbf{3}) \phi_s(\mathbf{2}) \phi_r(\mathbf{1}) \right)}_{w^{\mathcal{B}}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4})} \hat{\Psi}(\mathbf{2}) \hat{\Psi}(\mathbf{1}), \quad (8)$$

with the expectation value as follows:

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle = \int_{\mathbf{1234}} w^{\mathcal{B}}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}). \quad (9)$$

Since we wish to compare directly to Eq.(3), we integrate out two variables:

$$\begin{aligned} f_{\Psi^{\mathcal{B}}}(\mathbf{1}, \mathbf{2}) &= \int_{\mathbf{34}} w^{\mathcal{B}}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) \\ &= \int_{\mathbf{34}} \sum_{rstu} V_{rs}^{tu} \phi_t(\mathbf{4}) \phi_u(\mathbf{3}) \phi_s(\mathbf{2}) \phi_r(\mathbf{1}) \\ &\quad \sum_{mnpq} \Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}] \phi_p(\mathbf{4}) \phi_q(\mathbf{3}) \phi_n(\mathbf{2}) \phi_m(\mathbf{1}) \\ &= \sum_{mnpqrs} V_{rs}^{pq} \Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}] \phi_s(\mathbf{2}) \phi_r(\mathbf{1}) \phi_n(\mathbf{2}) \phi_m(\mathbf{1}), \end{aligned} \quad (10)$$

so that:

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle = \int_{\mathbf{12}} f_{\Psi^{\mathcal{B}}}(\mathbf{1}, \mathbf{2}) = \int_{\mathbf{12}} W_{\Psi^{\mathcal{B}}}(\mathbf{1}, \mathbf{2}) n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}), \quad (11)$$

where we define:

$$W_{\Psi^{\mathcal{B}}}(\mathbf{1}, \mathbf{2}) = f_{\Psi^{\mathcal{B}}}(\mathbf{1}, \mathbf{2}) / n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}). \quad (12)$$

We have hence defined an effective Coulomb interaction expressed in the basis \mathcal{B} , directly comparable to $1/r_{12}$. The interested reader will find a more in-depth discussion about $W_{\Psi^{\mathcal{B}}}$ in the Appendix A. We can plot those functions, see Figure 2, and see that recovering a quantitative interaction within a basis is difficult at short electron-electron range. This is closely linked to the wavefunctions found in Figure 1, where the cusp-less wavefunctions within a basis actually stem from an Hamiltonian with a non-diverging interaction, which is what we observe in the Figure below, with the effective, basis set limited, Coulomb interactions. The true Coulomb interaction is diverging and the corresponding true wavefunction does show a cusp. The physics missing from a description within a particular basis hence comes from a poor description of the short electron-electron range.

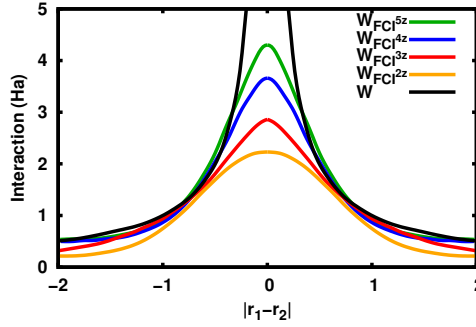


Figure 2: True Coulomb interaction and effective interactions as defined in Eq.(12) calculated, for the Helium atom, from wavefunctions at the FCI level and different Dunning basis sets. Note again that the long electron-electron range isn't particularly problematic, while the short electron-electron range is challenging, but improves by enlarging the basis set.

3 Parallel to range-separation

As will be made clear in the following, this sounds like “range-separation”. Range-separation will not be discussed at length here, but the idea in a nutshell is to calculate an energy as a sum of a wavefunction theory calculation performed with a non-diverging long-range Coulomb potential and of a DFT calculation

performed with the complementary short-range Coulomb potential. This aims at using both theories where they are good and it involves DFT functionals derived in the literature in the presence of the short-range Coulomb interaction.

The splitting into a short- and long-range component typically uses the “erf” function and involves a range-separation parameter μ :

$$\frac{1}{r_{12}} = \frac{\text{erf}(\mu r_{12})}{r_{12}} + \frac{1 - \text{erf}(\mu r_{12})}{r_{12}}. \quad (13)$$

The left of Figure 3 shows a plot of those three potentials: the short-range potential (in red) is a diverging potential that quickly goes to zero and is dominant under a range of $\sim 0.5/\mu$, while the long-range potential (in blue) is a non-diverging potential that dominates above a range of $\sim 0.5/\mu$. The range of those potential is hence governed by the value of μ . To make evident the close analogy between the long-range potential used in range-separation and the effective potential derived in the previous section, we show on the right of Figure 3 plots of long-range potentials with different parameter μ , on the same scale as Figure 2, which showed the effective potentials.

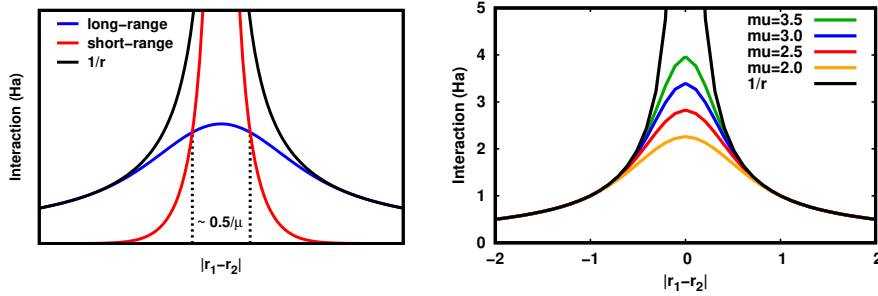


Figure 3: Left: Full-, long- and short-range potentials as used in range-separation. A parameter μ is used to control the range separation. Right: different μ parameters will (sort of) reproduce the different effective potentials derived in the previous section, showing how the parallel with range-separation arises (same scale as Figure 2).

Hence, if we are looking at:

$$E = E_{\text{wft}}^{\mathcal{B}} + E^{\mathcal{B}}[n], \quad (14)$$

where $E_{\text{wft}}^{\mathcal{B}}$ is calculated in an effective, basis-restricted, non-diverging potential, then $E^{\mathcal{B}}[n]$ is the correction stemming from the complementary potential. Deriving a new functional $E^{\mathcal{B}}[n]$ would require performing a uniform-electron gas calculation with the interaction complementary to $W_{\Psi^{\mathcal{B}}}$, which is challenging for various reasons (notably for example because the interaction is not translationally invariant or isotropic, which questions whether a uniform density could be obtained from it). Rather, since the effective, basis-restricted, non-diverging potential is a long-range potential, we can realize that the complementary potential must be a corresponding short-range potential and that the correction

$E^{\mathcal{B}}[n]$ will advantageously be derived using existing short-range functionals from the range-separation literature. In other words, we realize that the diverging Coulomb electron-electron interaction projected in a finite basis set ($W_{\Psi^{\mathcal{B}}}$) and the non-diverging long-range electron-electron interaction defined in a complete basis set ($\text{erf}(\mu r_{12})/r_{12}$) yield wavefunctions that qualitatively represent the same type of physics.

The idea is then to model the effective potential $W_{\Psi^{\mathcal{B}}}$ by a long-range potential with a basis set dependant local range-separation parameter (actually: a wavefunction dependant local range-separation parameter):

$$\tilde{W}_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2) \stackrel{\text{model}}{=} \frac{\text{erf}(\mu^{\mathcal{B}}(\mathbf{r}_1) r_{12})}{r_{12}}, \quad (15)$$

where the local value of the range-separation parameter $\mu^{\mathcal{B}}(\mathbf{r}_1)$ is chosen such that the values of the long-range interaction at coalescence and of the effective interaction at coalescence at point \mathbf{r}_1 are identical :

$$\tilde{W}_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_1) = W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_1) \iff \mu^{\mathcal{B}}(\mathbf{r}_1) = \frac{\sqrt{\pi}}{2} W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_1). \quad (16)$$

Hence the way the range-separation technology is adapted into a correction tailored to the basis set is by replacing the parameter μ in the (already existing) short-range functionals by a local function $\mu^{\mathcal{B}}$ fitted to represent the Coulomb interaction within the basis \mathcal{B} . As a result, the method does not involve a fixed parameter but a fitted function of space:

$$E^{\mathcal{B}}[n] = E^{\text{sr}}[n; \mu^{\mathcal{B}}(\mathbf{r})]. \quad (17)$$

In contrast with the functionals used in DFT or in range-separation, the correction functional $E^{\mathcal{B}}[n]$ is not universal: it depends on the basis set \mathcal{B} used to describe a specific system.

4 Practical implementation

We focus on the “short-range PBE” correlation functional:

$$E_{\text{PBE}}^{\text{sr}}[n; \mu] = \int n(\mathbf{r}) \epsilon_{\text{PBE}}^{\text{sr}}(\mathbf{r}; n, s, \zeta, \mu) d\mathbf{r}, \quad (18)$$

which depends on the density $n(\mathbf{r})$, the spin-polarization $\zeta(\mathbf{r}) = (n_{\alpha}(\mathbf{r}) - n_{\beta}(\mathbf{r}))/n(\mathbf{r})$, the reduced density gradient $s = |\nabla n(\mathbf{r})|/n^{4/3}(\mathbf{r})$ and on the parameter μ governing the range-separation. A program that has the usual PBE

functional ϵ_{PBE} at hand needs to implement the short-range functional as follow:

$$\epsilon_{\text{PBE}}^{\text{sr}}(\mathbf{r}; n, s, \zeta, \mu) = \frac{\epsilon_{\text{PBE}}(\mathbf{r}; n, s, \zeta)}{1 + \beta(\mathbf{r}; n, s, \zeta)\mu^3} \quad (19)$$

$$\beta(\mathbf{r}; n, s, \zeta) = \frac{3}{2\sqrt{\pi}(1 - \sqrt{2})} \frac{\epsilon_{\text{PBE}}(\mathbf{r}; n, s, \zeta)}{n^{(2)}(\mathbf{r})/n(\mathbf{r})} \quad (20)$$

$$n^{(2)} \sim n_{\text{UEG}}^{(2)}(\mathbf{r}; n, \zeta) = n^2(\mathbf{r})(1 - \zeta^2(\mathbf{r}))g_0(\mathbf{r}; n) = 4n_\alpha(\mathbf{r})n_\beta(\mathbf{r})g_0(\mathbf{r}; n), \quad (21)$$

where the on-top pair density of the uniform electron gas (UEG) uses the parametrization of the on-top pair-distribution function $g_0(\mathbf{r}; n)$ found in the literature. As seen in the equation for β , in the most general derivation, the on-top pair density of the current wavefunction would be used instead of $n_{\text{UEG}}^{(2)}$.

For the calculation of $\mu^{\mathcal{B}}$, since we are interested only in objects at electron-electron coalescence, the reduced-density matrix reduces to its opposite-spin contribution:

$$\Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}] = \langle \Psi^{\mathcal{B}} | \hat{a}_{p\uparrow}^\dagger \hat{a}_{q\downarrow}^\dagger \hat{a}_{n\downarrow} \hat{a}_{m\uparrow} | \Psi^{\mathcal{B}} \rangle \quad (22)$$

Moreover, since the difference between the use of $W_{\text{HF}^{\mathcal{B}}}$ and $W_{\text{FCI}^{\mathcal{B}}}$ is unnoticeable, the former is used to calculate $\mu^{\mathcal{B}}$, and the opposite-spin reduced density matrix reduces further to $\Gamma_{mn}^{pq}[\text{HF}] = 2\delta_{mp}\delta_{nq}\delta_{pi\uparrow}\delta_{qj\downarrow}$. This simplifies greatly the equations for $f_{\text{HF}^{\mathcal{B}}}$ and of course for $n_{\text{HF}^{\mathcal{B}}}^{(2)}$:

$$f_{\text{HF}^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_1) = 2 \sum_{pq} \sum_i^\alpha \sum_j^\beta \phi_p(\mathbf{r}_1) \phi_q(\mathbf{r}_1) V_{pq}^{ij} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \quad (23)$$

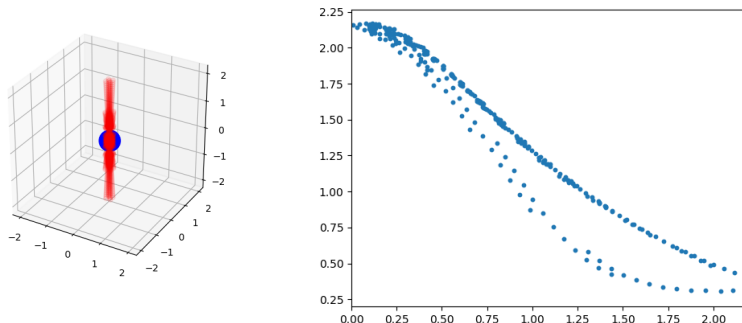
$$n_{\text{HF}^{\mathcal{B}}}^{(2)}(\mathbf{r}_1, \mathbf{r}_1) = 2 \sum_i^\alpha \sum_j^\beta \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) = 2n_\alpha(\mathbf{r}_1)n_\beta(\mathbf{r}_1). \quad (24)$$

A more involved version could implement the more costly Eqs. (6) and (10) as well as using the true on-top pair density in Eq.(20).

5 Plots of functions of space

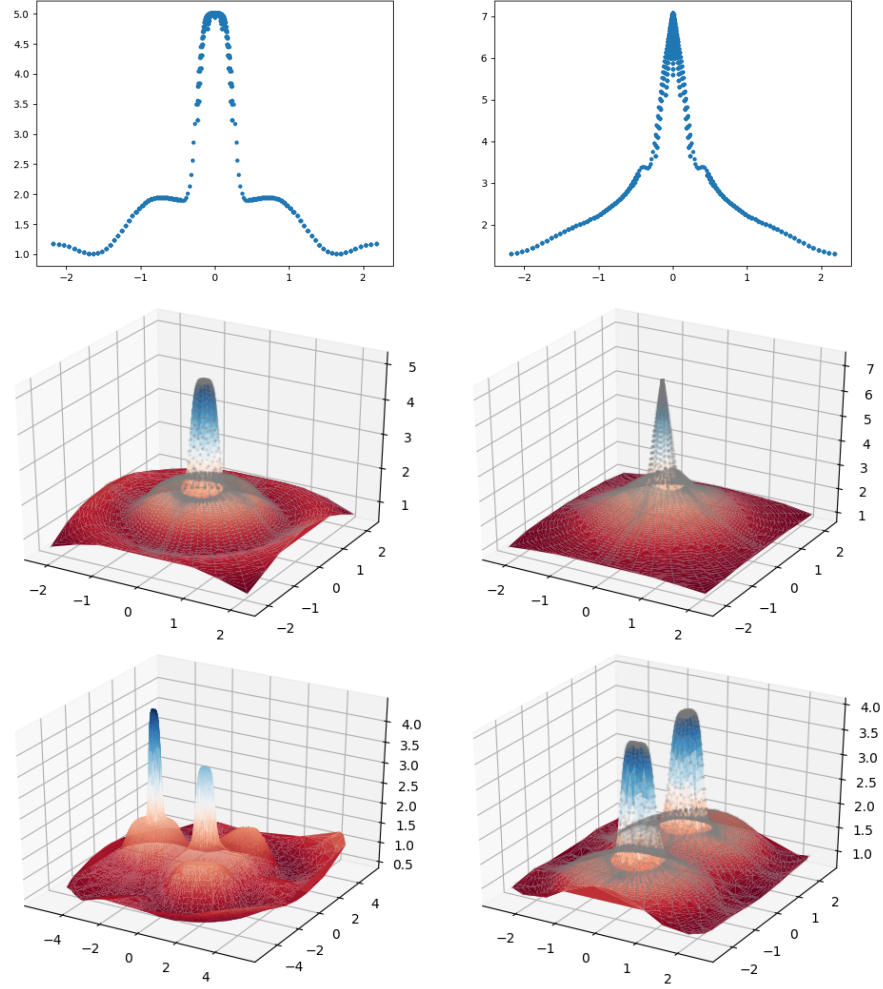
Effective interaction

We illustrate here that the effective interaction $W_{\Psi^{\mathcal{B}}}$ is not isotropic: on top of the fact that the coalescence values $W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_1)$ are not expected to be the same for all \mathbf{r}_1 , the values of $W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2)$ are not the same depending of the direction of \mathbf{r}_2 with respect to \mathbf{r}_1 .



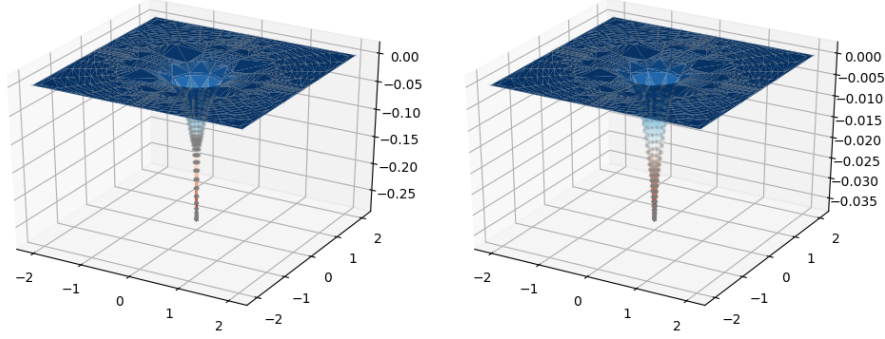
Local parameter

We can see that the magnitude of $\mu^{\mathcal{B}}$ increases with the basis set size. This is because the electron-electron interaction is better described by large basis sets, and less correction is needed. In this way, the local parameter can be seen as a measure of the incompleteness of a given basis set. Additionally (not displayed here), the maximal value was found to be reached when \mathbf{r} is at a nucleus, and $\mu^{\mathcal{B}}$ is generally highly nonuniform in space. This echoes the non-homogeneity of the description of the electron-electron interaction with atom-centered basis functions. Also, a large correction comes from bonding regions, highlighting the imperfect description of correlation effects in these regions with Gaussian basis sets. Finally, and most importantly for our purposes here, it was observed that the values of $\mu^{\mathcal{B}}$ are nearly undistinguishable when using HF or FCI wavefunction as $\Psi^{\mathcal{B}}$, which simplifies the intermediary objects involved (see Section 4).



PBE and short-range PBE functionals

We can compare the correlation hole modeled by the native PBE functional and by the short-range PBE functional using the basis set tailored range-separation parameter μ^B .



A Details about the effective interaction

From the mere restriction of the *operator* to the space spanned by the basis set \mathcal{B} , we have that:

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{ee} | \Psi^{\mathcal{B}} \rangle = \langle \Psi^{\mathcal{B}} | \hat{W}_{ee}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle, \quad (25)$$

which is really what makes the direct comparison of $W_{\Psi^{\mathcal{B}}}$ and $1/r_{12}$ valid, as:

$$\int_{\mathbf{12}} \frac{1}{r_{12}} n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}) = \int_{\mathbf{12}} W_{\Psi^{\mathcal{B}}}(\mathbf{1}, \mathbf{2}) n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}). \quad (26)$$

Note that this means that the integrands have the same integral, but this does not require the functions to be equal at each point, and there exist an infinite number of functions satisfying this property, meaning that the effective interaction is not uniquely defined. That being said, $W_{\Psi^{\mathcal{B}}}$ has compelling properties, for instance:

$$\lim_{\mathcal{B} \rightarrow \infty} W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_{12}} \quad (27)$$

$$\lim_{\mathcal{B} \rightarrow \infty} \hat{W}_{ee}^{\mathcal{B}} = \hat{W}_{ee} \quad (28)$$

$$\lim_{\mathcal{B} \rightarrow \infty} w^{\mathcal{B}}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) = w(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) \quad (29)$$

$$W_{\Psi^{\mathcal{B}}}(\mathbf{r}_2, \mathbf{r}_1) = W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2), \quad (30)$$

On the other hand, since \mathcal{B} is often atom-centered, the effective interaction is not going to be translationally invariant or isotropic, which means that it does not depend only on the r_{12} :

$$W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2) \neq W_{\Psi^{\mathcal{B}}}(r_{12}), \quad (31)$$

and the quality of the projected Coulomb operator and of the electron correlation effects are not expected to be spatially uniform. Moreover, as we saw in the main body of the document, since $f_{\Psi^{\mathcal{B}}}$ is obtained from a finite sum over bounded quantities, the value of the effective interaction at coalescence is finite

(provided the on-top pair density does not vanish at coalescence), but since the effective interaction is not translationally invariant, the value $W_{\Psi\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_1)$ has no reason to be independent of \mathbf{r}_1 . (As a matter of fact, the global shape of the effective interaction is qualitatively modified by changing the reference point \mathbf{r}_1 , which is a signature that the atom-centered basis set does not uniformly describe the Coulomb interaction at all points in space.)

B Why not just

What if we want to look at a wavefunction-independant effective Coulomb interaction:

$$\int_{\mathbf{12}} \frac{1}{r_{\mathbf{12}}} n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}) = \int_{\mathbf{12}} g(\mathbf{1}, \mathbf{2}) n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}) \quad (32)$$

where g would be the projection within the available basis \mathcal{B} of the two-dimensions Coulomb interaction:

$$\begin{aligned} g(\mathbf{1}, \mathbf{2}) &= \hat{P}^{\mathcal{B}} \frac{1}{r_{\mathbf{12}}} \\ &= \sum_{rs} c_{rs} \phi_r(\mathbf{1}) \phi_s(\mathbf{2}) \\ &= \sum_{rs} \langle \phi_r \phi_s | \frac{1}{\mathbf{r}} \rangle \phi_r(\mathbf{1}) \phi_s(\mathbf{2}) \\ &= \sum_{rs} \left(\int_{\mathbf{1}'\mathbf{2}'} \phi_r(\mathbf{1}') \frac{1}{r_{\mathbf{1}'\mathbf{2}'}} \phi_s(\mathbf{2}') \right) \phi_r(\mathbf{1}) \phi_s(\mathbf{2}) \end{aligned} \quad (33)$$

where the coefficients involved should exist in most codes since they are calculated for example in the course of a density-fitting calculation. Let's try to compare this to $W_{\Psi^{\mathcal{B}}} = f_{\Psi^{\mathcal{B}}} / n_{\Psi^{\mathcal{B}}}^{(2)}$. Starting with massaging f :

$$\begin{aligned} f_{\Psi^{\mathcal{B}}}(\mathbf{1}, \mathbf{2}) &= \sum_{mnpqrs} \Gamma_{mn}^{pq} [\Psi^{\mathcal{B}}] V_{rs}^{pq} \phi_s(\mathbf{2}) \phi_r(\mathbf{1}) \phi_n(\mathbf{2}) \phi_m(\mathbf{1}) \\ &= \sum_{mnpqrs} \int_{\mathbf{1}'\mathbf{2}'} \Gamma_{mn}^{pq} [\Psi^{\mathcal{B}}] \left(\phi_p(\mathbf{1}') \phi_q(\mathbf{2}') \frac{1}{r_{\mathbf{1}'\mathbf{2}'}} \phi_r(\mathbf{1}') \phi_s(\mathbf{2}') \right) \\ &\quad \times \phi_s(\mathbf{2}) \phi_r(\mathbf{1}) \phi_n(\mathbf{2}) \phi_m(\mathbf{1}) \\ &= \sum_{rs} \left(\int_{\mathbf{1}'\mathbf{2}'} n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{2}', \mathbf{1}') \phi_r(\mathbf{1}') \frac{1}{r_{\mathbf{1}'\mathbf{2}'}} \phi_s(\mathbf{2}') \right) \phi_r(\mathbf{1}) \phi_s(\mathbf{2}) \end{aligned} \quad (34)$$

we get to the effective interaction itself as:

$$W_{\Psi^{\mathcal{B}}}(\mathbf{1}, \mathbf{2}) = \sum_{rs} \left(\int_{\mathbf{1}'\mathbf{2}'} \frac{n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{2}', \mathbf{1}')}{n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{2}, \mathbf{1})} \phi_r(\mathbf{1}') \frac{1}{r_{\mathbf{1}'\mathbf{2}'}} \phi_s(\mathbf{2}') \right) \phi_r(\mathbf{1}) \phi_s(\mathbf{2}) \quad (35)$$

which is what $g(\mathbf{1}, \mathbf{2})$ is, but for the factor of the quotient of pair densities... I can't quite see right away why one would do one rather than the other.

A more conceptual comparison

Remember the expression for the true Coulomb operator:

$$\hat{W}_{ee} = \int_{\mathbf{1234}} \hat{\Psi}^\dagger(\mathbf{4}) \hat{\Psi}^\dagger(\mathbf{3}) \left(\frac{1}{r_{\mathbf{12}}} \delta_{\mathbf{14}} \delta_{\mathbf{23}} \right) \hat{\Psi}(\mathbf{2}) \hat{\Psi}(\mathbf{1}) \quad (36)$$

with expectation value:

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle = \int_{\mathbf{12}} \frac{1}{r_{\mathbf{12}}} n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}) \quad (37)$$

Now, applying the approximation that $\hat{\Psi}(\mathbf{1}) = \sum_p \phi_p(\mathbf{1}) \hat{a}_p$ to the true Coulomb operator gets us the effective operator that we know from second quantization:

$$\begin{aligned} \hat{W}_{\text{ee}}^{\text{effective}} &= \sum_{pqrs} \hat{a}_s^\dagger \hat{a}_r^\dagger \int_{\mathbf{1234}} \left(\phi_s(\mathbf{4}) \phi_r(\mathbf{3}) \left(\frac{1}{r_{\mathbf{12}}} \delta_{\mathbf{14}} \delta_{\mathbf{23}} \right) \phi_q(\mathbf{2}) \phi_p(\mathbf{1}) \right) \hat{a}_q \hat{a}_p \\ &= \sum_{pqrs} V_{pq}^{sr} \hat{a}_s^\dagger \hat{a}_r^\dagger \hat{a}_q \hat{a}_p \end{aligned} \quad (38)$$

with expectation value:

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\text{effective}} | \Psi^{\mathcal{B}} \rangle = \int_{\mathbf{1234}} w(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) \quad (39)$$

which prompts the derivation of $W_{\Psi^{\mathcal{B}}}$ in Giner's papers. (This is, by the way, the quantity we actually calculate in the basis-correction code: the one stemming from the second-quantized expression above.) I feel like writing $g(\mathbf{1}, \mathbf{2}) = \hat{P}^{\mathcal{B}} \frac{1}{r_{\mathbf{12}}}$ amounts to defining:

$$\hat{W}_{\text{ee}}^g = \int_{\mathbf{1234}} \hat{\Psi}^\dagger(\mathbf{4}) \hat{\Psi}^\dagger(\mathbf{3}) (g(\mathbf{1}, \mathbf{2}) \delta_{\mathbf{14}} \delta_{\mathbf{23}}) \hat{\Psi}(\mathbf{2}) \hat{\Psi}(\mathbf{1}) \quad (40)$$

with expectation value:

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle = \int_{\mathbf{12}} g(\mathbf{1}, \mathbf{2}) n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{1}, \mathbf{2}) \quad (41)$$

(this is our starting point above) whereas defining a projection of the four-dimension true Coulomb interaction for some reason is really the way to go:

$$\begin{aligned} g(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) &= \hat{P}^{\mathcal{B}} \left(\frac{1}{\mathbf{r}} \delta \delta \right) \\ &= \sum_{pqrs} \langle \phi_p \phi_q \phi_r \phi_s | \frac{1}{r_{\mathbf{12}}} \delta_{\mathbf{14}} \delta_{\mathbf{23}} \rangle \phi_p(\mathbf{1}) \phi_q(\mathbf{2}) \phi_r(\mathbf{3}) \phi_s(\mathbf{4}) \end{aligned} \quad (42)$$

which of course makes us go in circles since:

$$\langle \phi_p \phi_q \phi_r \phi_s | \frac{1}{\mathbf{r}} \delta \delta \rangle = \int_{\mathbf{1234}} \phi_p(\mathbf{1}) \phi_q(\mathbf{2}) \phi_r(\mathbf{3}) \phi_s(\mathbf{4}) \frac{1}{r_{\mathbf{12}}} \delta_{\mathbf{14}} \delta_{\mathbf{23}} = V_{pq}^{sr} \quad (43)$$

which yields again:

$$g(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}) = \sum_{pqrs} V_{pq}^{sr} \phi_p(\mathbf{1}) \phi_q(\mathbf{2}) \phi_r(\mathbf{3}) \phi_s(\mathbf{4}) \quad (44)$$

which is why the derivation from them is needed.