Rudiments of Exact Exchange in DFT

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Exact exchange in DFT is defined as being the exchange energy in Hartree-Fock *form* evaluated with the Kohn-Sham (KS) orbitals, $\varphi_i(\mathbf{r})$, [1–3] that is

$$E_x := -\frac{1}{2}\sum_{i,j}^{N}{}' \int d\mathbf{r}d\mathbf{r}' \frac{\varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ . \tag{1}$$

Recall that the KS orbitals themselves are *defined* as being those which minimize the single-determinantal expectation value of the N-electron kinetic energy operator and produce the stipulated density

$$n(\mathbf{r}) = \sum_{j}^{N} |\varphi_j(\mathbf{r})|^2 \ . \tag{2}$$

It is fairly common also to define the non-local exact-exchange potential as

$$v_x^{NL}(\mathbf{r},\mathbf{r}') := -\sum_{j}^{N} \frac{\varphi_j(\mathbf{r})\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ . \tag{3}$$

To remain within the KS conceptual framework requires finding the *local* exact exchange potential,

$$v_x(\mathbf{r}) := \frac{\delta E_x}{\delta n} \ . \tag{4}$$

Since there is not an explicit expression for taking the required functional derivative of Eq. (1), an indirect but simple route is used. This exploits the fact that the functional derivative chain rule allows one to write the expression for the needed derivative in terms of the ones that can be taken explicitly. We have

$$\int d\mathbf{r}' \left[\frac{\delta E_x}{\delta n(\mathbf{r}')}\frac{\delta n(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})}\right] = \sum_j \int d\mathbf{r}' \left[\frac{\delta E_x}{\delta \varphi_j(\mathbf{r}')}\frac{\delta \varphi_j(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})} + cc\right] \ . \tag{5}$$

Here v_{KS} is the full KS potential. The functional derivative we need is the first factor on the LHS. The second factor on that side is the so-called KS response function

$$\chi(\mathbf{r},\mathbf{r}') := \frac{\delta n(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})} \tag{6}$$

Since it is a first functional derivative with respect to the change in a potential, it is given exactly in first order perturbation theory in terms of the KS orbitals and eigenvalues themselves, to wit,

$$\chi(\mathbf{r},\mathbf{r}') = \sum_{\ell}\sum_{i\neq\ell}\left[\frac{\varphi_\ell^*(\mathbf{r})\varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')\varphi_\ell(\mathbf{r}')}{\varepsilon_\ell - \varepsilon_i} + cc\right] \ . \tag{7}$$

Now address the RHS of Eq. (5). Again from perturbation theory,

$$\frac{\delta \varphi_j(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})} = \sum_{k\neq j} \varphi_k(\mathbf{r}')\frac{\varphi_k^*(\mathbf{r})\varphi_j(\mathbf{r})}{\varepsilon_j - \varepsilon_k} \ . \tag{8}$$

Together with Eq. (3) this yields

$$\begin{aligned} t_x(\mathbf{r}) &:= \sum_j \int d\mathbf{r}' \left[\frac{\delta E_x}{\delta \varphi_j(\mathbf{r}')}\frac{\delta \varphi_j(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})} + cc\right] \\ &= \sum_j \sum_{k\neq j}\left[\frac{\varphi_k^*(\mathbf{r})\varphi_j(\mathbf{r}) \int d\mathbf{r}'\varphi_j^*(\mathbf{r}')v_x^{NL}(\mathbf{r},\mathbf{r}')\varphi_k(\mathbf{r}')}{\varepsilon_j - \varepsilon_k} + cc\right] \ . \end{aligned} \tag{9}$$

Putting it all together, one must invert the integral equation

$$\int d\mathbf{r}'\chi(\mathbf{r},\mathbf{r}')v_x(\mathbf{r}') = t_x(\mathbf{r}) \ , \tag{10}$$

with χ and t_x given above. Thus there is an iterative self-consistent procedure, because those two quantities depend upon KS orbitals and eigenvalues which they also determine. In the case of finite systems, the actual inversion of Eq. (10) has proven to have some subtle numerical challenges, beyond the scope of this note.

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