Alternative treatment of the singularity in the Exact Exchange energy of periodic systems

James Spencer and Ali Alavi
CUC^3

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Reference determinant for molecules

$$\begin{aligned} E_0 =& \langle D_{\mathbf{0}}|H|D_{\mathbf{0}}\rangle \\ =& \sum_{i}^{N} h_i + \sum_{i<j}^{N} [\langle ij|ij\rangle - \langle ij|ji\rangle] \end{aligned}$$

Exchange energy is defined as:

$$E_x = -\frac{1}{2}\sum_{ij}^{N}\langle ij|ji\rangle$$

where i and j refer to spin-orbitals.
For a spin-restricted calculation, this becomes:

$$E_x = -\sum_{ab}^{N/2}\langle ab|ba\rangle$$

What about a periodic system?

Suppose we have a set of one-particle orbitals

$$\phi_{v\mathbf{k}}(\mathbf{r})$$

computed over a k-point mesh with N_k kpoints which span the FBZ.

$$\phi_{v\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u_{v\mathbf{k}}(\mathbf{r})$$

$u_{v\mathbf{k}}$ is periodic over the primitive unit cell (with volume Ω).

$\phi_{v\mathbf{k}}$ is periodic over the crystal cell (with volume $N_k\Omega$).

Exact exchange in extended systems

By analogy the exact exchange energy, E_x, per unit cell:

$$
\begin{aligned}
E_x &= -\frac{1}{N_k}\sum_{v\mathbf{k}}^{\text{occ}}\sum_{w\mathbf{k}'}^{\text{occ}}\langle v\mathbf{k}w\mathbf{k}'|w\mathbf{k}'v\mathbf{k}\rangle \\
&= -\frac{1}{N_k}\sum_{v\mathbf{k}}^{\text{occ}}\sum_{w\mathbf{k}'}^{\text{occ}}\int\int\frac{\phi^*_{v\mathbf{k}}(\mathbf{r})\phi^*_{w\mathbf{k}'}(\mathbf{r}')\phi_{w\mathbf{k}'}(\mathbf{r})\phi_{v\mathbf{k}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= -\frac{4\pi}{N_k\Omega}\sum_{v\mathbf{k}}^{\text{occ}}\sum_{w\mathbf{k}'}^{\text{occ}}\sum_{\mathbf{G}}\frac{Y_{v\mathbf{k},w\mathbf{k}'}(\mathbf{G})Y_{w\mathbf{k}',v\mathbf{k}}(-\mathbf{G})}{|\mathbf{G}-\mathbf{k}+\mathbf{k}'|^2}
\end{aligned}
$$

$$
\begin{aligned}
Y_{v\mathbf{k},w\mathbf{k}'}(\mathbf{G}) &= \frac{1}{N_k\Omega}\int_{N_k\Omega}d\mathbf{r}e^{-i\mathbf{G}.\mathbf{r}}\phi^*_{v\mathbf{k}}(\mathbf{r})\phi_{w\mathbf{k}'}(\mathbf{r}) \\
&= \frac{1}{N_k\Omega}\int_{N_k\Omega}d\mathbf{r}e^{-i(\mathbf{G}+\mathbf{k}-\mathbf{k}').\mathbf{r}}u^*_{v\mathbf{k}}(\mathbf{r})u_{w\mathbf{k}'}(\mathbf{r})
\end{aligned}
$$

Exact exchange singularity

$$E_x = -\frac{4\pi}{N_k\Omega}\sum_{v\mathbf{k}}^{\text{occ}}\sum_{w\mathbf{k}'}^{\text{occ}}\sum_{\mathbf{G}}\frac{Y_{v\mathbf{k},w\mathbf{k}'}(\mathbf{G})Y_{w\mathbf{k}',v\mathbf{k}}(-\mathbf{G})}{|\mathbf{G}-\mathbf{k}+\mathbf{k}'|^2}$$

Singular terms are those for which: $\mathbf{k} = \mathbf{k}'$ and $v = w$ and $\mathbf{G} = 0$. (Note $\mathbf{k}$ and $\mathbf{k}'$ are confined to be within FBZ.)

Singularity is integrable only in the infinite $\mathbf{k}$-point limit where the sums $\Sigma_{\mathbf{k}} \to \frac{\Omega}{(2\pi)^3}\int d\mathbf{k}$.

Auxiliary functions I

A function, $f(\mathbf{k})$, which:

- is periodic within the reciprocal lattice
- diverges as $\frac{1}{\mathbf{k}^2}$ as $\mathbf{k} \longrightarrow 0$ and is smooth elsewhere
- is even

can be added to the singular terms (cancelling out the singularity) and then integrated out separately (ideally analytically).

Relies on existence of suitable auxiliary function for a given lattice type.

fcc, analytic: Gygi and Balderschi, PRB 34 4405 (1986)
various: Wenzien, Cappellini and Bechstedt, PRB 51 14701 (1995)
general: Carrier, Rohra and Görling, PRB 75 205126 (2007)

Auxiliary functions II

$$E_x = -\frac{4\pi}{N_k\Omega}\sum_{v\mathbf{k}}^{\text{occ}}\sum_{w\mathbf{k}'\neq\mathbf{k}}^{\text{occ}}\sum_{\mathbf{G}}\frac{Y_{v\mathbf{k},w\mathbf{k}'}(\mathbf{G})Y_{w\mathbf{k}',v\mathbf{k}}(-\mathbf{G})}{|\mathbf{G}-\mathbf{k}+\mathbf{k}'|^2}$$
$$-\frac{4\pi}{N_k\Omega}\sum_{\mathbf{k}}\sum_{vw}^{\text{occ}}\sum_{\mathbf{G}\neq\mathbf{0}}\frac{Y_{v\mathbf{k},w\mathbf{k}}(\mathbf{G})Y_{w\mathbf{k},v\mathbf{k}}(-\mathbf{G})}{|\mathbf{G}|^2}$$
$$+N_v(\tilde{F}-F),$$

where

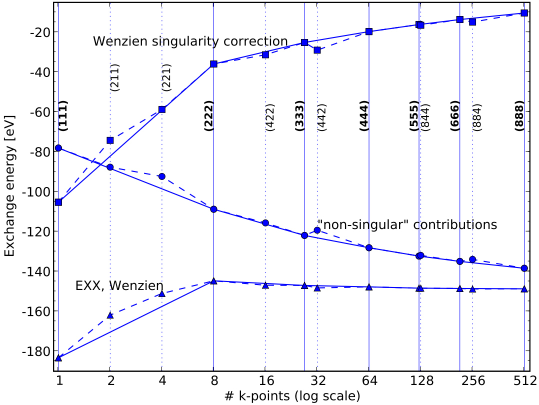
$$\tilde{F} = \frac{4\pi}{N_k\Omega}\sum_{\mathbf{k}}\sum_{\mathbf{k}'\neq\mathbf{k}} f(\mathbf{k}-\mathbf{k}')$$

and

$$F = \frac{1}{2\pi^2}\int_{\text{BZ}} f(\mathbf{k})d\mathbf{k}.$$

Auxiliary functions III

e.g. for α-SiC, using the Wenzien auxiliary function:



Truncated Coulomb potential

$$v_{\mathrm{atten.}}(\mathbf{r}) = \begin{cases} \frac{1}{|\mathbf{r}|} & |\mathbf{r}| \leq R_c \\ 0 & \text{otherwise.} \end{cases}$$

So the equivalent exchange integrals are:

$$\langle v\mathbf{k}w\mathbf{k}'|w\mathbf{k}'v\mathbf{k}\rangle_{\mathrm{atten}} = \int_{N_k\Omega}\int_{\Omega_{R_c}(\mathbf{r})} \frac{\phi^*_{v\mathbf{k}}(\mathbf{r})\phi^*_{w\mathbf{k}'}(\mathbf{r}')\phi_{w\mathbf{k}'}(\mathbf{r})\phi_{v\mathbf{k}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

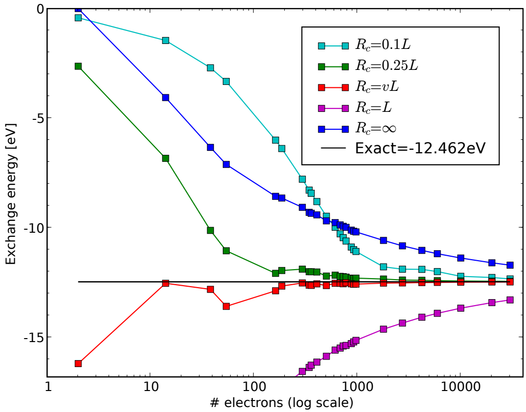
Simple modification to the potential kernel:

$$E_x = -\frac{4\pi}{N_k\Omega}\sum_{v\mathbf{k}}^{\mathrm{occ}}\sum_{w\mathbf{k}'}^{\mathrm{occ}}\sum_{\mathbf{G}} \frac{Y_{v\mathbf{k},w\mathbf{k}'}(\mathbf{G})Y_{w\mathbf{k}',v\mathbf{k}}(-\mathbf{G})}{|\mathbf{G}-\mathbf{k}+\mathbf{k}'|^2}[1-\cos(|\mathbf{G}-\mathbf{k}+\mathbf{k}'|R_c)].$$

Potential no longer contains any singularities.

JS and AA, PRB (in press, May 2008).

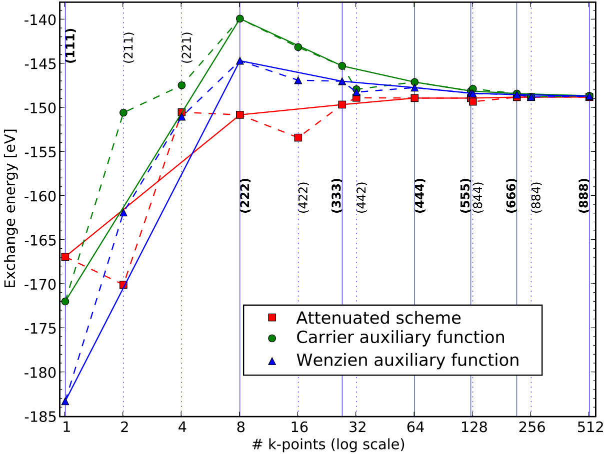
UEG



L: lattice parameter.
$\frac{4}{3}\pi(vL)^3 = L^3$.
Calculations: Alex Thom.

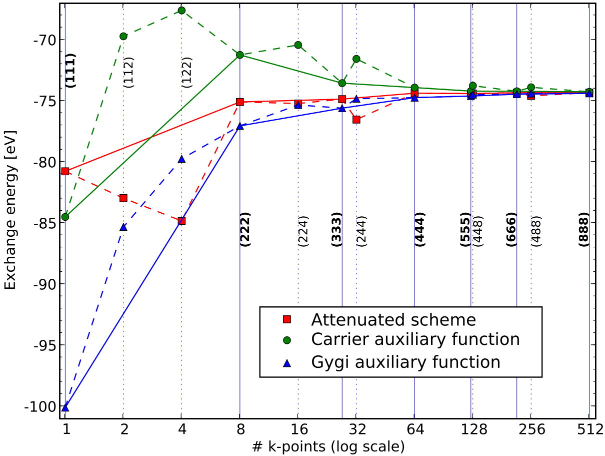
α-SiC

Hexagonal close-packed ($a = 3.076$Å, $c = 5.048$Å), 80 Rydberg cutoff.



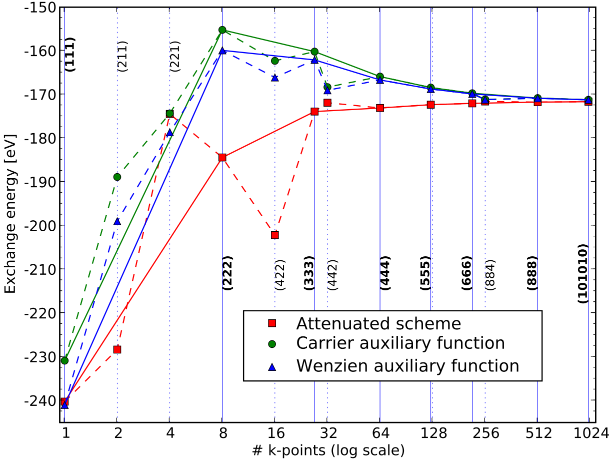
β-SiC

Face-centred cubic ($a = 4.3596$Å), 80 Rydberg cutoff.



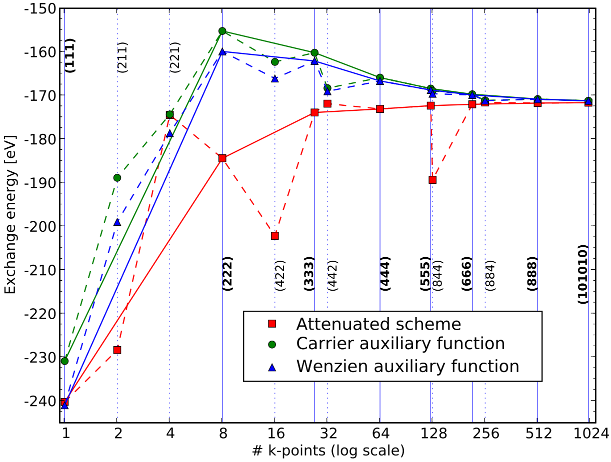
Graphite

Hexagonal close-packed ($a = 2.464$Å, $c = 6.711$Å), 80 Rydberg cutoff.



Diamond

Face-centred cubic ($a = 3.3676$Å), 80 Rydberg cutoff.



Exact exchange and periodic boundary conditions

- Infinite system: pair-wise exchange between all electrons.
- Artificial periodicity of the crystal cell imposed on the system.
  $\Rightarrow$ Forces electrons in different crystal cells to be distinguishable.
- Calculating exchange integrals over the Wigner–Seitz cell allows only exchange between electrons in the same crystal cell.

Reference determinant for extended systems

$$E_0 = \langle D_{\mathbf{0}} | H | D_{\mathbf{0}} \rangle$$

Extended systems:

$$\begin{aligned} E_0 =& 2\sum_{v\mathbf{k}} h_{v\mathbf{k}} + \sum_{v\mathbf{k}} \sum_{w,\mathbf{k}'} \left[2\langle v\mathbf{k}w\mathbf{k}' | v\mathbf{k}w\mathbf{k}' \rangle - \langle v\mathbf{k}w\mathbf{k}' | w\mathbf{k}'v\mathbf{k} \rangle_{\mathrm{atten}} \right] \\ =& 2\sum_{v\mathbf{k}} h_{v\mathbf{k}} + \sum_{v\mathbf{k}} \sideset{}{'}\sum_{w\mathbf{k}'} \left[2\langle v\mathbf{k}w\mathbf{k}' | v\mathbf{k}w\mathbf{k}' \rangle - \langle v\mathbf{k}w\mathbf{k}' | w\mathbf{k}'v\mathbf{k} \rangle_{\mathrm{atten}} \right] \\ & + \sum_{v\mathbf{k}} \langle v\mathbf{k}v\mathbf{k} | v\mathbf{k}v\mathbf{k} \rangle + \sum_{v\mathbf{k}} \xi_{v\mathbf{k}} \end{aligned}$$

where the prime ' indicates $w \neq v$ when $\mathbf{k}' = \mathbf{k}$.

Periodic interactions

$$U_{\text{ee}} = \frac{1}{2} \sum_{\mathbf{L}} \sum_{i,j}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{L}|}$$

The prime ' indicates that when $L = 0$, $i \neq j$, i.e.
An electron interacts with its periodic images but not itself.
Obtain a "ξ"-like correction which is wavefunction-dependent:

$$\begin{aligned}
\xi_{v\mathbf{k}} &= \langle v\mathbf{k}v\mathbf{k}| \sum_{\mathbf{L}\neq 0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{L}|} |v\mathbf{k}v\mathbf{k}\rangle \\
&= \langle v\mathbf{k}v\mathbf{k}| \sum_{\mathbf{L}} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{L}|} |v\mathbf{k}v\mathbf{k}\rangle - \langle v\mathbf{k}v\mathbf{k}| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |v\mathbf{k}v\mathbf{k}\rangle_{\text{cell}} \\
&= \langle v\mathbf{k}v\mathbf{k}| \sum_{\mathbf{L}} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{L}|} |v\mathbf{k}v\mathbf{k}\rangle - \langle v\mathbf{k}v\mathbf{k}| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |v\mathbf{k}v\mathbf{k}\rangle_{\text{atten}}
\end{aligned}$$