Pseudopotentials for QMC

Richard Needs

University of Cambridge, UK

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Core-valence partition

Assign orbitals to core or valence

Li: \[ 1s^2 \quad | \quad 2s^1 \]

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Si: \[ 1s^2 \quad 2s^2 \quad 2p^6 \quad | \quad 3s^2 \quad 3p^2 \]

Fe: \[ 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad | \quad 3d^6 \quad 4s^2 \]

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Partition is also in energy and space
Density matrix approach of Acioli and Ceperley

“Pseudopotentials from correlated wave functions”
Acioli and Ceperley, J Chem Phys 100, 8169 (1994)

\[ \rho(\mathbf{r}, \mathbf{r}') = N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \ldots, \mathbf{r}_N) \, d\mathbf{r}_2 \ldots d\mathbf{r}_N \]

Write in terms of eigenvectors and eigenfunctions of \( \rho(\mathbf{r}, \mathbf{r}') \)

\[ \rho(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{\infty} n_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}') \quad 0 \leq n_i \leq 2 \]

Norm-conservation

\[ \rho(\mathbf{r}, \mathbf{r}') = \rho^{PS}(\mathbf{r}, \mathbf{r}') \quad r, r' \geq r_c \]

Need accurate all-electron wave function for atom
Helium: \( \rho^{PS}(\mathbf{r}, \mathbf{r}') \) only correct when both electrons are outside \( r_c \)
Pseudopotentials with local DFT

All-electron orbitals $\phi_{l}^{\text{AE}}(r)$ eigenvalues $\epsilon_{l}^{\text{AE}}$

Pseudo orbitals $\phi_{l}^{\text{PS}}(r)$ eigenvalues $\epsilon_{l}^{\text{PS}}$

For valence electrons insist that:

$$
\epsilon_{l}^{\text{PS}} = \epsilon_{l}^{\text{AE}}
$$

$$
\phi_{l}^{\text{PS}}(r) = \phi_{l}^{\text{AE}}(r) \quad r > r_c
$$

$$
\begin{bmatrix}
-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l + 1)}{2r^2} + V_{l}^{\text{AE}}
\end{bmatrix} \phi_{l}^{\text{AE}} = \epsilon_{l}^{\text{AE}} \phi_{l}^{\text{AE}}
$$

$$
\begin{bmatrix}
-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l + 1)}{2r^2} + V_{l}^{\text{PS}}
\end{bmatrix} \phi_{l}^{\text{PS}} = \epsilon_{l}^{\text{PS}} \phi_{l}^{\text{PS}}
$$

Must therefore have $V_{l}^{\text{PS}}(r) = V_{l}^{\text{AE}}(r) \quad r > r_c$

Use norm conservation and smoothness for $\phi_{l}^{\text{PS}}(r < r_c)$, invert SE for $V_{l}^{\text{PS}}$
Pseudopotentials within Hartree-Fock theory

Similar to local DFT – with a twist!

Exchange interaction is very long ranged

Inverting the Schrödinger equation in local DFT gives

\[ V_{l}^{PS} \simeq -\frac{Z_{\text{ion}}}{r} \quad r \to \infty \]

but in Hartree-Fock theory get

\[ V_{l}^{PS} \simeq A - \frac{Z_{\text{ion}} + B}{r} + \mathcal{O}(r^{-2}) \quad r \to \infty \]


Total energy not defined for an extended system
Can apparently deal with the problem without much loss of accuracy
Pseudopotentials from fitting to excitation energies

Don’t need to invert the Schrödinger equation to make a pseudopotential

Can fit to excitation energies obtained from:
(1) Hartree-Fock theory
(2) A correlated theory
(3) Experiment

Issue: excitation energies may be very large
Lowest excitation energy of H is $1s \rightarrow 2s$ which costs $\sim 8$ eV
Could fit to correlated energies with a perturbing potential
Empirical Pseudopotential I


\[ \phi_{III}(r) \propto W_{x,l+1/2} \left( \frac{2Z_{\text{ion}}r}{x} \right) \quad , \quad x = \frac{Z_{\text{ion}}}{\sqrt{2\epsilon}} \]

\( W \equiv \) Whittaker function of the second kind
Consider single electrons outside of the core in \( s, p, \) or \( d \) levels

\[
V_{\text{III}}^{\text{PS}}(r) = -\frac{Z_{\text{ion}}}{r}
\]

For \( r_c > r < r_0 \) take

\[
V_{\text{II}}^{\text{PS}}(r) = -\frac{Z_{\text{ion}}}{r} - \frac{\alpha}{2r^4}
\]

Energy \( \epsilon_l \) to remove the electron available experimentally for most atoms

Get charge density norms for each orbital from DFT

Make corrections to the energies \( \epsilon_l \) (roughly -0.05 eV for Si) and norms (roughly 0.002 electrons for Si) to allow for fact that \( \epsilon_l \) come from 3+ ions
Integrate Schrödinger equation at energy $\epsilon_l$ from $r_o$ to $r_c$ to get $\phi_{II}(r)$

Si atom: $r_{cs} = 1.75$ a.u., $r_{cp} = 1.80$ a.u., $r_{cd} = 2.0$ a.u., $r_0 = 20.17$ a.u.

Invert Schrödinger equation to get $\phi_I(r)$ and hence $V_{I}^{PS}(r)$ as in DFT

Gave best results in atomic excitation tests, also good results in recent solid state calculations of silicon in diamond and $\beta$-tin structures

Problems? Need a more accurate potential in region II
Current level of testing insufficient
Testing HF pseudopotentials

Test two sets of pseudos:

55 molecules of the G2 set with the CRYSTAL code
Atoms: H, Li, Be, C, N, O, F, Na, Si, P, S, Cl
Max number of atoms in a molecule = 8
Gaussian basis sets optimised for each molecule
Normally 17 basis functions per atom, sometimes have to reduce a bit

Compare spherical atoms from CRYSTAL from integrating HF on a grid:
MAD = 0.0012 eV per atom
Compare atomisation energies with all-electron HF of O’Neill and Gill Mol Phys 103, 763 (2005)
MAD (Trail and Needs) = 0.26 eV per molecule
MAD (Burkatzki, Filippi, Dolg) = 0.24 eV per molecule
(NB, THESE ARE NOT FINISHED YET)

The molecules are almost all overbound

Conclusion !*&(?!+)*(*@!?@:¿ @