Projector Augmented Wave Formulation of Optimized Effective Potential Density Functional Theory - PAW–OEP

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Introduction

The optimized effective potential (OEP) or exact exchange (EXX) formalism has recently received renewed interest as a method which can improve the accuracy of density functional theory with respect to core-valence exchange-correlation functionals. Since the Projector Augmented Wave (PAW) formalism\(^\text{1}\) enables an accurate treatment of the important multiple moments as well as the core–valence contributions to the exchange interaction, it is a natural choice for implementing OEP within an efficient pseudopotential-like scheme. This paper presents a progress report on our PAW-OEP project, focusing on spherically symmetric atoms and in particular on the transition metals, where the frozen-core approximation is inadequate because of the important multipole moments as well as the core–valence interaction.

The formulation of the frozen-core approximation within the OEP formalism is somewhat more complicated than the frozen-core approximation for density-exchange correlation functionals. We have found the following scheme to give reasonable results. First, since the exchange energy can be divided into valence and core contributions, we assume that the OEP potential can be divided into two terms:

\[ V_{\text{OEP}}(\mathbf{r}) = V_{\text{valence}}(\mathbf{r}) + V_{\text{core}}(\mathbf{r}) \]

where the core contribution is fixed for the reference configuration and the valence contribution is updated as the electronic configuration and valence orbitals are modified. The valence OEP \( V_{\text{valence}}(\mathbf{r}) \) is determined iteratively using the valence shift function

\[ \delta E_{\text{valence}} = \sum_n \langle \phi_n | f_{\text{valence}} | \phi_n \rangle \]

where the modified "valence-valence" auxiliary function \( f_{\text{valence}}(\mathbf{r}) \) is a solution to theinhomogeneous equation

\[ \delta E_{\text{core}} = \sum_n \langle \phi_n | f_{\text{core}} | \phi_n \rangle \]

where the modified "core-core" auxiliary function \( f_{\text{core}}(\mathbf{r}) \) is a solution to the inhomogeneous equation

\[ \delta E_{\text{total}} = \sum_n \langle \phi_n | f_{\text{total}} | \phi_n \rangle \]

In this expression, \( f_{\text{total}}(\mathbf{r}) \) denotes the total OEP contribution to the PAW exchange as expressed in Eq. (3). Using the reference configuration, it is clear that the frozen-core and all-electron results are identical because of the relationships

\[ \langle \phi_n | f_{\text{total}} | \phi_n \rangle = \langle \phi_n | f_{\text{core}} | \phi_n \rangle + \langle \phi_n | f_{\text{valence}} | \phi_n \rangle \]

A practical algorithm for determining \( V_{\text{valence}}(\mathbf{r}) \) and \( V_{\text{core}}(\mathbf{r}) \) for a reference configuration of atoms is similar to the OEP equation algorithm described above. In this case, the orbitals \( \{\phi_n\} \) and Hartree and exchange potentials are fixed, so steps 2–4 can be omitted. Steps 2–4 are used with the valence contribution to determine \( V_{\text{valence}}(\mathbf{r}) \) and valence-valence auxiliary function \( f_{\text{valence}}(\mathbf{r}) \) to determine the valence OEP \( \delta E_{\text{valence}} \).

Two examples of valence and core partitioning of the OEP are shown in Fig. 1 below for N and Fe in their reference configurations. For N, the frozen-core was chosen to be \( 2p^4 \). For Fe, two different sets of results are shown, comparing the results of treating the valence 3d electrons as valence (with Ar core) or including the "semi-core" with the valence states 3d\(\uparrow / \downarrow\) (with Ne core). Apparently, the later choice results in smoother functional forms for \( V_{\text{valence}}(\mathbf{r}) \) and \( \delta E_{\text{valence}} \).

\[ \delta E_{\text{core}} = \sum_n \langle \phi_n | f_{\text{core}} | \phi_n \rangle \]

For determining excited states in the frozen-core approximation, we can again use a modified version of the OEP iteration algorithm. In this case, all steps are used to determine a new \( \{\phi_n\}_0 \), with new valence orbitals \( \{\phi_n\}_{\text{valence}}(\mathbf{r}) \), using Eqs. 3 and 9. An example is shown in the graph below.

For all cases there is an agreement to the OEP results. PAW–OEP formulation

The formulation for frozen-core OEP can be directly adapted for use in the PAW method. The PAW Hamiltonian has the form

\[ H^\text{PAW} = H + \sum_n |\phi_n\rangle \langle \phi_n| \]

where the pseudo-Hartree–Fock Hamiltonian \( H \) contains the pseudo-potential of the form

\[ V_{\text{PAW}}(\mathbf{r}) = V_{\text{valence}}(\mathbf{r}) + V_{\text{core}}(\mathbf{r}) \]

The effective of core exchange potential \( V_{\text{core}}(\mathbf{r}) \) is represented in the pseudopotential function \( V_{\text{PAW}}(\mathbf{r}) \) as well as the pseudovalence exchange potential. The summation in Eq. 15 includes into basis functions \( \{\phi_n\} \) and the on-center matrix elements \( E_{\text{core}} \). It will also contain contributions from the core-core exchange potentials \( V_{\text{core}}(\mathbf{r}) \) as well as various contributions from the valence exchange potentials \( V_{\text{valence}}(\mathbf{r}) \) and \( V_{\text{core}}(\mathbf{r}) \). The PAW form of the Kohn–Sham equations (3) for the pseudowavefunctions \( |\psi_n\rangle \) in

\[ \left( H^\text{PAW} - \varepsilon_n \right) \psi_n = 0 \]

Here \( \varepsilon_n \) denotes the pseudopotential eigenvalue. The equations for the auxiliary function \( f_{\text{core}}(\mathbf{r}) \), analogous to Eq. (9), would take the form

\[ \left( H^\text{PAW} - \varepsilon_n - \delta E_{\text{core}} \right) f_{\text{core}} = 0 \]

In this expression, the only valence-valence interactions to the PAW exchange functional \( L_{\text{valence}}(\mathbf{r}) \) contribute. The corresponding PAW shift function would then take the form analogous to Eq. (10),

\[ \delta E_{\text{valence}} = \sum_n \langle \phi_n | f_{\text{valence}} | \phi_n \rangle \]

for splatting \( V_{\text{valence}}(\mathbf{r}) \) and

\[ \delta E_{\text{core}} = \sum_n \langle \phi_n | f_{\text{core}} | \phi_n \rangle \]

for splatting the on-center matrix elements \( E_{\text{core}} \).

References


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