

Projector Augmented Wave Formulation of Exact Exchange Density Functional Theory – PAW-EXX

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Introduction

The optimized effective potential (OEP) or exact exchange (EXX) formalism has recently received renewed attention as a method which can improve the accuracy of density functional theory with its ability to treat orbital-dependent functionals such as the Fock exchange and orbital-dependent correlation functionals.^{1–3} Since the Projector Augmented Wave (PAW) formalism⁴ enables an accurate treatment of the important core-valence contributions to the exchange interaction,¹ it is a natural choice for implementing EXX within an efficient pseudopotential-like scheme. This poster presents an early progress report on our PAW-EXX project. Concentrating, for the moment, on an exchange-only approach we show results from our atomic structure code and outline a PAW-EXX formalism.

Gradient search method for EXX

A convenient formulation of the exact exchange method has been developed by several authors^{2,3} as a constrained minimization problem. The function to be minimized is the total energy of the system including kinetic, nuclear, Hartree, and exchange terms:

$$E = E_T + E_N + E_H + E_x. \quad (1)$$

Here, the exchange energy is expressed in terms of Kohn-Sham orbitals $\{\psi_n(\mathbf{r})\}$ as

$$E_x(\{\psi_n(\mathbf{r})\}) = -\frac{e^2}{2} \sum_{nm} \delta_{\sigma_n \sigma_m} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\psi_n(\mathbf{r}')\psi_m^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2)$$

The ground state of the system can be found by minimizing $E(\{\psi_n(\mathbf{r})\})$ with the constraint that the orbitals are eigenstates of the Kohn-Sham equations:

$$H^{KS} \psi_n = E_n \psi_n \quad \text{where} \quad H^{KS} \equiv T + V \quad \text{and} \quad V = V_N + V_H + V_x. \quad (3)$$

The potential terms represent the nuclear, Hartree, and exchange contributions, respectively. In the EXX formulation, while the nuclear and Hartree potentials can be determined from functional derivatives with respect to the electronic density $\rho(\mathbf{r})$,

$$V_N(\mathbf{r}) \equiv \frac{\delta E_N}{\delta \rho(\mathbf{r})} \quad \text{and} \quad V_H(\mathbf{r}) \equiv \frac{\delta E_H}{\delta \rho(\mathbf{r})}, \quad (4)$$

the exact exchange potential $V_x(\mathbf{r})$ is determined as part of the constrained minimization. Following Hyman, Stiles and Zangwill,² it is convenient to map the problem into the minimization of an auxiliary function with the help of Lagrange multipliers:

$$F(\{\psi_n(\mathbf{r})\}, \{g_n(\mathbf{r})\}, \{E_n\}, V_x(\mathbf{r}), \{\lambda_n\}) = E(\{\psi_n\}) - \sum_n \lambda_n (\langle \psi_n | \psi_n \rangle - 1) - \sum_n \left(\langle g_n | H^{KS} - E_n | \psi_n \rangle + \langle \psi_n | H^{KS} - E_n | g_n \rangle \right). \quad (5)$$

The minimization of the auxiliary function F results in the following relations. The Lagrange multiplier function $g_n(\mathbf{r})$ is a solution to an inhomogeneous differential equation

$$(H^{KS} - E_n)g_n(\mathbf{r}) = \frac{\partial E_x}{\partial \psi_n(\mathbf{r})} - V_x(\mathbf{r})\psi_n(\mathbf{r}) - U_n \psi_n(\mathbf{r}), \quad \text{where} \quad U_n \equiv \langle \psi_n | \frac{\partial E_x}{\partial \psi_n} \rangle - \langle \psi_n | V_x | \psi_n \rangle, \quad (6)$$

with the condition $\langle g_n | \psi_n \rangle + \langle \psi_n | g_n \rangle = 0$. The functions $\{g_n\}$ are in turn related to the gradient of the auxiliary function F with respect to the exchange function according to

$$\frac{\partial F}{\partial V_x(\mathbf{r})} = -\sum_n (g_n^*(\mathbf{r})\psi_n(\mathbf{r}) + g_n(\mathbf{r})\psi_n^*(\mathbf{r})) = 0. \quad (7)$$

Gradient search algorithm for self-consistent EXX potential

$\alpha = 1$; Set initial potential $V^\alpha = V_N + V_H^\alpha + V_x^\alpha$.

Do

1. Solve: $(T + V^\alpha)\psi_n^{\alpha+1} = E_n^{\alpha+1}\psi_n^{\alpha+1}$.

2. Calculate: $\frac{\partial F^{\alpha+1}}{\partial V^\alpha} \equiv -G^{\alpha+1}(\mathbf{r})$

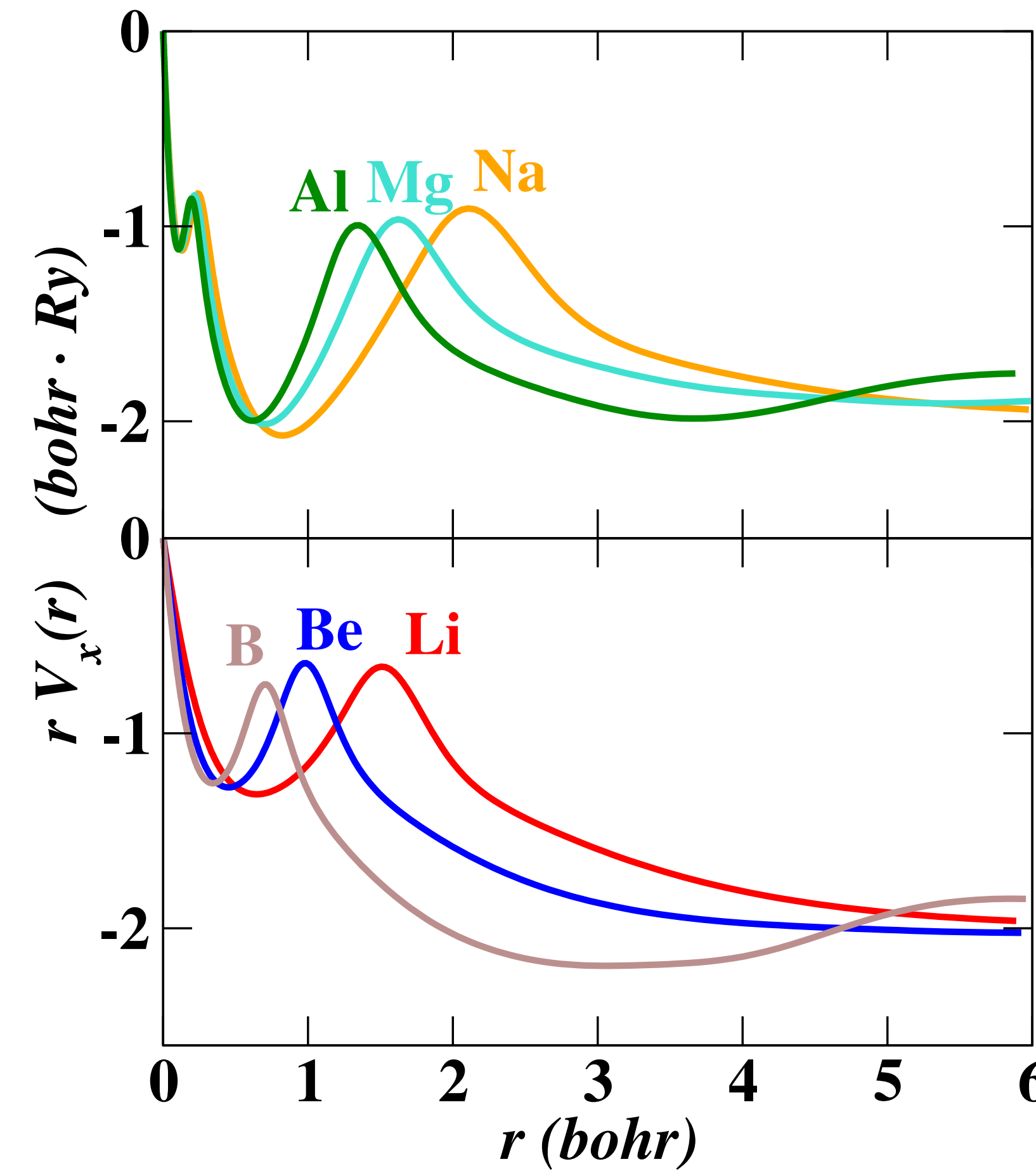
3. If $|G^{\alpha+1}| < \epsilon \implies \text{CONVERGED}$

4. Else Update: $V^{\alpha+1} = V^\alpha + \lambda G^{\alpha+1}$; $\alpha = \alpha + 1$

EndDo

At the end of this procedure, $V_x = V^\alpha - V_N - V_H^\alpha$. We have programmed this algorithm for spherical atoms and the results agree well with literature values as shown in the Table and Figure.

Some examples of atomic exact exchange potentials



EXX ground-state energies (Ry)

Atom	Present Work	Previous Work ^a	LDA
H	-1.0000	-1.0000	-0.8913
He	-5.7234	-5.7234	-5.6689
Li	-14.8648	-14.8650	-14.6692
Be	-29.1449	-29.1448	-28.8929
B	-49.0555	-49.0566	-48.6864
F	-198.8155	-198.8184	-198.1934
Ne	-257.0908	-257.0908	-256.4598
Na	-323.7126	-323.7132	-322.8724
Mg	-399.2232	-399.2232	-398.2706
Al	-483.7463	-483.7466	-482.6224
Cl	-918.9541	-918.9552	-917.3166
Ar	-1053.6244	-1053.6244	-1051.8796
K	-1198.3175	-1198.3182	-1196.3877
Ca	-1353.5038	-1353.5038	-1351.4706

^aGrabo, Kreibich, Kurth, & Gross, in Ansimov, ed. *Strong coulomb correlations in electronic structure calculations*. (Gordon and Breach, 2000), pg. 203.

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PAW-EXX formulation

PAW calculations⁴ require a set of basis and projector functions which can be denoted $|\phi_i^a(\mathbf{r})\rangle$, $|\tilde{\phi}_i^a(\mathbf{r})\rangle$, and $|\tilde{p}_i^a(\mathbf{r})\rangle$, for the all-electron basis functions, pseudopotential basis functions, and projector functions, respectively. Here the “ a ” superscript denotes the atomic site index, and the “ i ” subscript represents the atomic quantum numbers n_i , l_i , and m_i for a spherical atom. In the PAW formulation, all calculations are performed in terms of smoothed pseudowavefunctions $\tilde{\psi}_n(\mathbf{r})$. The corresponding all-electron wavefunctions can then be estimated with the PAW transformation

$$\psi_n(\mathbf{r}) = \tilde{\psi}_n(\mathbf{r}) + \sum_{ai} (\phi_i^a(\mathbf{r}) - \tilde{\phi}_i^a(\mathbf{r})) \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle. \quad (8)$$

The pseudowavefunctions are normalized in terms of an overlap operator

$$\langle \tilde{\psi}_n | \mathbf{O} | \tilde{\psi}_m \rangle = \delta_{nm}, \quad \text{where} \quad \mathbf{O} \equiv \mathbf{1} + \sum_{aij} |\tilde{p}_i^a\rangle \left(\langle \phi_i^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{\phi}_j^a \rangle \right) \langle \tilde{p}_j^a|. \quad (9)$$

In the PAW formulation, the total energy of the system can be expressed in terms of the pseudowavefunctions with the general form

$$E^{PAW}(\{\tilde{\psi}_n(\mathbf{r})\}) = \tilde{E} + \sum_a (E^a - \tilde{E}^a). \quad (10)$$

Here, \tilde{E} represents contributions from smooth functions which extend over all space, while the $E^a - \tilde{E}^a$ contributions are confined to “augmentation spheres” of radius r_a^a at each atomic site, representing all-electron corrections to the energy in the vicinity of each atom. As recently shown,⁵ the exchange contributions to the energy can also be represented in the form

$$E_x^{PAW}(\{\tilde{\psi}_n(\mathbf{r})\}) = \tilde{E}_x + \sum_a (E_x^a - \tilde{E}_x^a). \quad (11)$$

In particular, the core-valence contributions can be represented in the E^a term through the use of the all-electron basis functions $\{\phi_i(\mathbf{r})\}$. The Kohn-Sham equations in the PAW formulation have the form:

$$H^{PAW} |\tilde{\psi}_n\rangle = E_n \mathbf{O} |\tilde{\psi}_n\rangle, \quad \text{where} \quad H^{PAW} \equiv \tilde{H} + \sum_{aij} |\tilde{p}_i^a\rangle D_{ij}^a \langle \tilde{p}_j^a|. \quad (12)$$

In this expression, \tilde{H} is a smooth pseudo-Hamiltonian representing the interactions throughout all space, while the D_{ij}^a matrix elements provide corrections to the Hamiltonian interactions in the vicinity of each atomic site a . The exact exchange potential contributes in three types of terms in this formulation. Within the smooth pseudo-Hamiltonian \tilde{H} , there will be a corresponding pseudo-exchange potential $\tilde{V}_x(\mathbf{r})$. In addition, for each atomic center, there will be atomic exchange potentials $V_x^a(\mathbf{r})$ for the all-electron and $\tilde{V}_x^a(\mathbf{r})$ for the pseudopotential contributions. These last two terms will contribute to D_{ij}^a matrix elements in the form:

$$[V_x^a]_{ij} \equiv \langle \phi_i^a | V_x^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{V}_x^a | \tilde{\phi}_j^a \rangle. \quad (13)$$

Consequently, the auxiliary function to be minimized should take the form:

$$F^{PAW}(\{\tilde{\psi}_n(\mathbf{r})\}, \{\tilde{g}_n(\mathbf{r})\}, \{E_n\}, \tilde{V}_x(\mathbf{r}), V_x^a(\mathbf{r}), \tilde{V}_x^a(\mathbf{r}), \{\lambda_n\}) = E^{PAW}(\{\tilde{\psi}_n\}) - \sum_n \lambda_n (\langle \tilde{\psi}_n | \mathbf{O} | \tilde{\psi}_n \rangle - 1) - \sum_n \left(\langle \tilde{g}_n | H^{PAW} - E_n \mathbf{O} | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_n | H^{PAW} - E_n \mathbf{O} | \tilde{g}_n \rangle \right). \quad (14)$$

The minimization of the auxiliary function F^{PAW} results in the following relations. The smooth Lagrange multiplier function $\tilde{g}_n(\mathbf{r})$ is a solution to the inhomogeneous differential equation

$$(H^{PAW} - E_n \mathbf{O}) \tilde{g}_n(\mathbf{r}) = \frac{\partial E^{PAW}}{\partial \tilde{\psi}_n(\mathbf{r})} - \tilde{V}_x(\mathbf{r}) \tilde{\psi}_n(\mathbf{r}) - \sum_{aij} \tilde{p}_i^a(\mathbf{r}) [V_x^a]_{ij} \langle \tilde{p}_j^a | \tilde{\psi}_n \rangle - U_n \mathbf{O} \tilde{\psi}_n(\mathbf{r}). \quad (15)$$

Here the constant U_n is given by $U_n \equiv \langle \tilde{\psi}_n | \frac{\partial E^{PAW}}{\partial \tilde{\psi}_n} \rangle - \langle \tilde{\psi}_n | \tilde{V}_x | \tilde{\psi}_n \rangle - \sum_{aij} \langle \tilde{\psi}_n | \tilde{p}_i^a \rangle [V_x^a]_{ij} \langle \tilde{p}_j^a | \tilde{\psi}_n \rangle$, and the orthogonality condition is given by $\langle \tilde{g}_n | \mathbf{O} | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_n | \mathbf{O} | \tilde{g}_n \rangle = 0$. The gradients of the PAW auxiliary function with respect to the exchange potentials are given by

$$\frac{\partial F^{PAW}}{\partial \tilde{V}_x^a(\mathbf{r})} = -\sum_n \left(\tilde{g}_n^*(\mathbf{r}) \tilde{\psi}_n(\mathbf{r}) + \tilde{g}_n(\mathbf{r}) \tilde{\psi}_n^*(\mathbf{r}) \right) \quad (16)$$

and

$$\frac{\partial F^{PAW}}{\partial V_x^a(\mathbf{r})} = -\sum_{nij} \left(\langle \tilde{g}_n | \tilde{p}_i^a \rangle \langle \tilde{p}_j^a | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_n | \tilde{p}_i^a \rangle \langle \tilde{p}_j^a | \tilde{g}_n \rangle \right) \phi_i^{a*}(\mathbf{r}) \phi_j^a(\mathbf{r}), \quad (17)$$

$$\frac{\partial F^{PAW}}{\partial \tilde{V}_x^a(\mathbf{r})} = \sum_{nij} \left(\langle \tilde{g}_n | \tilde{p}_i^a \rangle \langle \tilde{p}_j^a | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_n | \tilde{p}_i^a \rangle \langle \tilde{p}_j^a | \tilde{g}_n \rangle \right) \tilde{\phi}_i^{a*}(\mathbf{r}) \tilde{\phi}_j^a(\mathbf{r}). \quad (18)$$