

Introduction

The optimized effective potential (OEP) or exact exchange (EXX) formalism has recently received renewed attention¹ 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. Since the Projector Augmented Wave (PAW) formalism² enables an accurate treatment of the important multipole moments as well as the core-valence contributions to the exchange interaction,³ it is a natural choice for implementing OEP within an efficient pseudopotential-like scheme. This poster presents a progress report on our PAW-OEP project, focusing on spherically symmetric atoms and including Fock exchange only. As a necessary first step, we have developed a frozen core approximation to the all-electron OEP formalism. From a reference configuration, we can partition the optimized effective potential into a “frozen” core contribution $V_x^{\text{core}}(\mathbf{r})$ and a valence contribution $V_x^{\text{vale}}(\mathbf{r})$ that adjusts to changes in the valence configuration. In assessing the accuracy of the approximation, we have calculated atomic excitation energies for elements across the periodic table, finding the frozen core errors to have a somewhat larger magnitude, and to depend differently on the atomic shell structure in comparison with density-dependent exchange-correlation functionals. The formalism for calculating $V_x^{\text{vale}}(\mathbf{r})$ can be directly adapted for use in the PAW method.

All-electron atomic OEP equations

The basic OEP equations can be derived⁴ as a constrained minimization problem to determine Kohn-Sham orbitals $\phi_n(\mathbf{r})$ and to minimize the total energy of the system:

$$E_{\text{tot}}[\{\phi_n(\mathbf{r})\}] = E_T + E_N + E_H + E_x, \quad (1)$$

where the right hand side terms correspond to the kinetic energy, the electron-nuclear energy, the electron-electron Coulomb repulsion and the Fock exchange energy, respectively. The Fock exchange energy takes the form:

$$E_x[\{\phi_n(\mathbf{r})\}] = -\frac{e^2}{2} \sum_{mm'} \delta_{\sigma_n \sigma_{m'}} \int d^3r \int d^3r' \frac{\phi_n^*(\mathbf{r}) \phi_m(\mathbf{r}) \phi_n(\mathbf{r}') \phi_m^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2)$$

where the summation includes all occupied orbitals having the same spin component σ_n . The orbitals $\{\phi_n(\mathbf{r})\}$ must be eigenstates of the Kohn-Sham equations:

$$H_{KS} \phi_n = \varepsilon_n \phi_n \quad \text{where} \quad H_{KS} = T + V \quad \text{and} \quad V = V_N + V_H + V_x, \quad (3)$$

where the first two potential contributions represent the nuclear potential and the Hartree (Coulomb) potential, while the last term is the OEP which must be determined. In general, $V_x(\mathbf{r})$ is determined iteratively by converging the “shift” function⁴⁻⁵

$$S(\mathbf{r}) = -\sum_n \{g_n^*(\mathbf{r}) \phi_n(\mathbf{r}) + g_n(\mathbf{r}) \phi_n^*(\mathbf{r})\} \rightsquigarrow 0. \quad (4)$$

In this expression the auxiliary functions $\{g_n(\mathbf{r})\}$ are solutions to inhomogeneous equations of the form

$$(H_{KS} - \varepsilon_n) g_n(\mathbf{r}) = \frac{\delta E_x}{\delta \phi_n^*} - V_x(\mathbf{r}) \phi_n(\mathbf{r}) - \bar{U}_v \phi_n(\mathbf{r}) - \sum_{m \neq n} \lambda_{nm} \phi_m(\mathbf{r}) \quad (5)$$

where

$$\bar{U}_v \equiv \langle \phi_n | \frac{\delta E_x}{\delta \phi_n^*} \rangle - \langle \phi_n | V_x | \phi_n \rangle \quad \text{and} \quad \lambda_{nm} \equiv \langle \phi_m | \frac{\delta E_x}{\delta \phi_n^*} \rangle - \langle \phi_m | V_x | \phi_n \rangle. \quad (6)$$

The last term of Eq. (5) is a new contribution, which we find useful in some cases to stabilize the auxiliary function $g_n(\mathbf{r})$ with the constraint that $\langle g_n | \phi_m \rangle = 0$.

In practice, these equations are solved using two nested iteration loops.

OEP iteration algorithm

$\alpha = 0$; Guess $V_x^\alpha(\mathbf{r})$

Do

1. For given $V_x^\alpha(\mathbf{r})$, iteratively solve Kohn-Sham equations (3) for self-consistent orbitals $\{\phi_n(\mathbf{r})\}$ and Hartree potential $V_H(\mathbf{r})$.
2. For these orbitals, solve for auxiliary functions $\{g_n(\mathbf{r})\}$ and determine the shift function $S(\mathbf{r})$, according to Eq. (4).
3. If $|S(\mathbf{r})| \leq \epsilon \implies$ CONVERGED
4. Else use $S(\mathbf{r})$ to update $V_x^\alpha(\mathbf{r}) \rightarrow V_x^{\alpha+1}(\mathbf{r})$; $\alpha = \alpha + 1$

EndDo

Frozen-core atomic OEP equations

Implicit in the PAW formalism (or any pseudopotential formalism) is the assumption that the states occupied by core electrons of atoms in a material can be well approximated as “frozen” and numerical attention is focused on describing the rearrangements of the valence electrons within the material.⁶ Von Barth and Gelatt⁷ analyzed the frozen-core approximation for density-dependent exchange-correlation functionals and found the error to be quite small. In this case, the core orbitals $\{\phi_c(\mathbf{r})\}_{c \in \text{core}}$ and their corresponding electron density are “frozen” at their values for a reference configuration, while the valence orbitals $\{\phi_v(\mathbf{r})\}_{v \in \text{vale}}$ and their corresponding electron density are optimized for each new electron configuration.

The formulation of the frozen-core approximation within the OEP formalism is somewhat more complicated than the frozen-core approximation for density-dependent 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:

$$V_x(\mathbf{r}) = V_x^{\text{core}}(\mathbf{r}) + V_x^{\text{vale}}(\mathbf{r}), \quad (7)$$

where the core contribution is fixed for the reference configuration and the valence contribution is updated as the electron configuration and valence orbitals $\{\phi_v(\mathbf{r})\}$ change. The valence OEP $V_x^{\text{vale}}(\mathbf{r})$ is determined iteratively using the valence shift function

$$S_v(\mathbf{r}) = -\sum_{v \in \text{vale}} \{g_v^*(\mathbf{r}) \phi_v(\mathbf{r}) + g_v(\mathbf{r}) \phi_v^*(\mathbf{r})\}, \quad (8)$$

where the modified “valence-valence” auxiliary function $g_v^v(\mathbf{r})$ is a solution to the inhomogeneous equation

$$(H_{KS} - \varepsilon_v) g_v^v(\mathbf{r}) = \frac{\delta E_x^{\text{vv}}}{\delta \phi_v^*} - V_x^{\text{vale}}(\mathbf{r}) \phi_v(\mathbf{r}) - \bar{U}_v \phi_v(\mathbf{r}) - \sum_{m \neq v} \lambda_{vm} \phi_m(\mathbf{r}). \quad (9)$$

In this expression, E_x^{vv} denotes the pure valence contributions to the Fock exchange as expressed in Eq. (2). The derivation of these results implies that there is a core shift function of the form

$$S_c(\mathbf{r}) = -\sum_{c \in \text{core}} \{g_c^*(\mathbf{r}) \phi_c(\mathbf{r}) + g_c(\mathbf{r}) \phi_c^*(\mathbf{r})\} - \sum_{v \in \text{vale}} \{g_v^*(\mathbf{r}) \phi_v(\mathbf{r}) + g_v(\mathbf{r}) \phi_v^*(\mathbf{r})\}, \quad (10)$$

where the modified “core-valence” auxiliary function $g_c^c(\mathbf{r})$ is a solution to the inhomogeneous equation

$$(H_{KS} - \varepsilon_c) g_c^c(\mathbf{r}) = \frac{\delta E_x^{\text{cv}}}{\delta \phi_c^*} - V_x^{\text{core}}(\mathbf{r}) \phi_c(\mathbf{r}) - \bar{U}_c \phi_c(\mathbf{r}) - \sum_{m \neq c} \lambda_{cm} \phi_m(\mathbf{r}). \quad (11)$$

In this expression, E_x^{cv} denotes the core-valence interaction contributions to the Fock exchange as expressed in Eq. (2). For the reference configuration, it is clear that the frozen-core and all-electron results are identical because of the relationships

$$g_v(\mathbf{r}) = g_v^v(\mathbf{r}) + g_c^c(\mathbf{r}) \quad \text{and} \quad S(\mathbf{r}) = S_v(\mathbf{r}) + S_c(\mathbf{r}). \quad (12)$$

A practical algorithm for determining $V_x^{\text{vale}}(\mathbf{r})$ and $V_x^{\text{core}}(\mathbf{r})$ for a reference configuration of atom is similar to the OEP iteration algorithm described above. In this case, the orbitals $\{\phi_n(\mathbf{r})\}$ and Hartree potential are fixed, so step #1 can be omitted. Steps 2-4 are used with the valence shift function $S_v(\mathbf{r})$ and valence-valence auxiliary function $g_v^v(\mathbf{r})$ to determine the valence OEP, $V_x^{\text{vale}}(\mathbf{r})$.

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 $1s^2$. For Fe, two different sets of results are shown, comparing the results of treating the states $3d4s$ as valence (with Ar core) or including the “semi-core” with the valence states – $3s3p3d4s$ (with Ne core). Apparently, the later choice results in smoother functional forms for $V_x^{\text{vale}}(\mathbf{r})$ and $V_x^{\text{core}}(\mathbf{r})$.

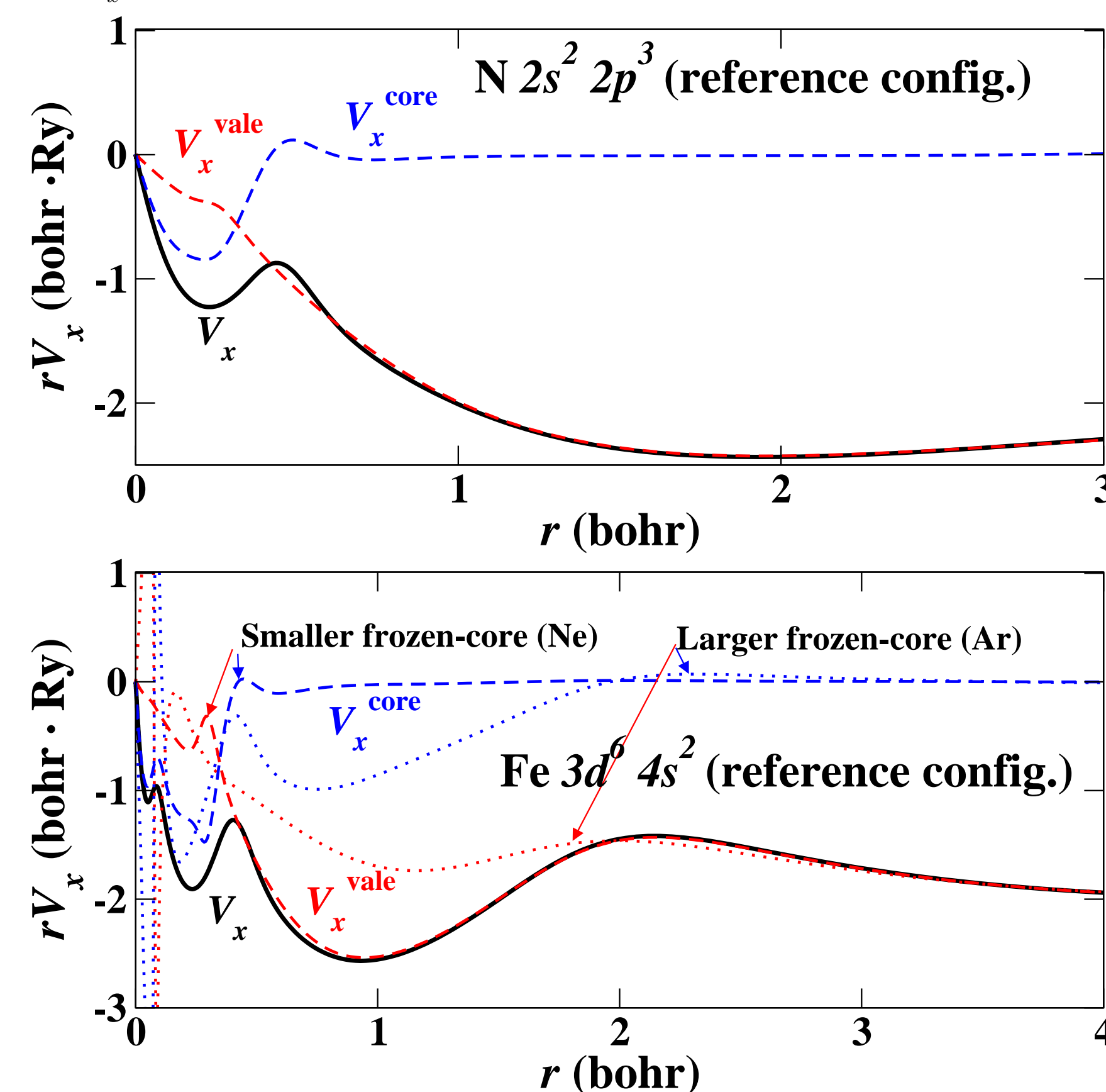


FIG. 1 Example of frozen-core partitioning of OEP for N and Fe in their reference configurations.

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 4 steps are used to determine a new $V_x^{\text{vale}}(\mathbf{r})$, with new valence orbitals $\phi_v(\mathbf{r})$, using Eqs. 8 and 9. An examples is shown in the graph below.

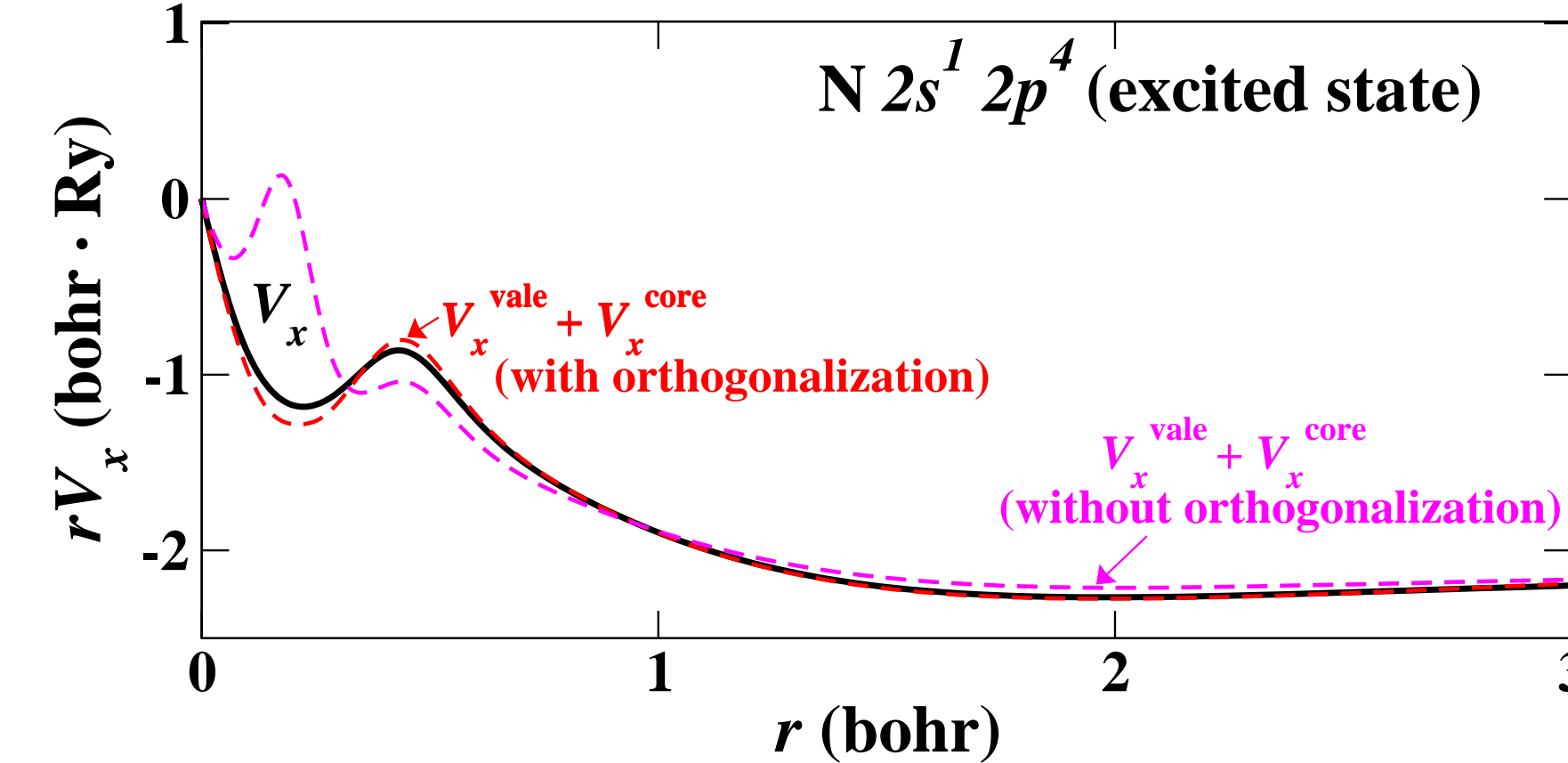


FIG. 2 Example of frozen-core calculation of an excited state of N relative to the $2s^2 2p^3$ reference configuration, comparing the effects of the orbital orthogonalization terms λ_{vm} . In this case, including the orbital orthogonalization terms stabilizes the calculation.

Some all-electron and frozen-core atomic excitation energies

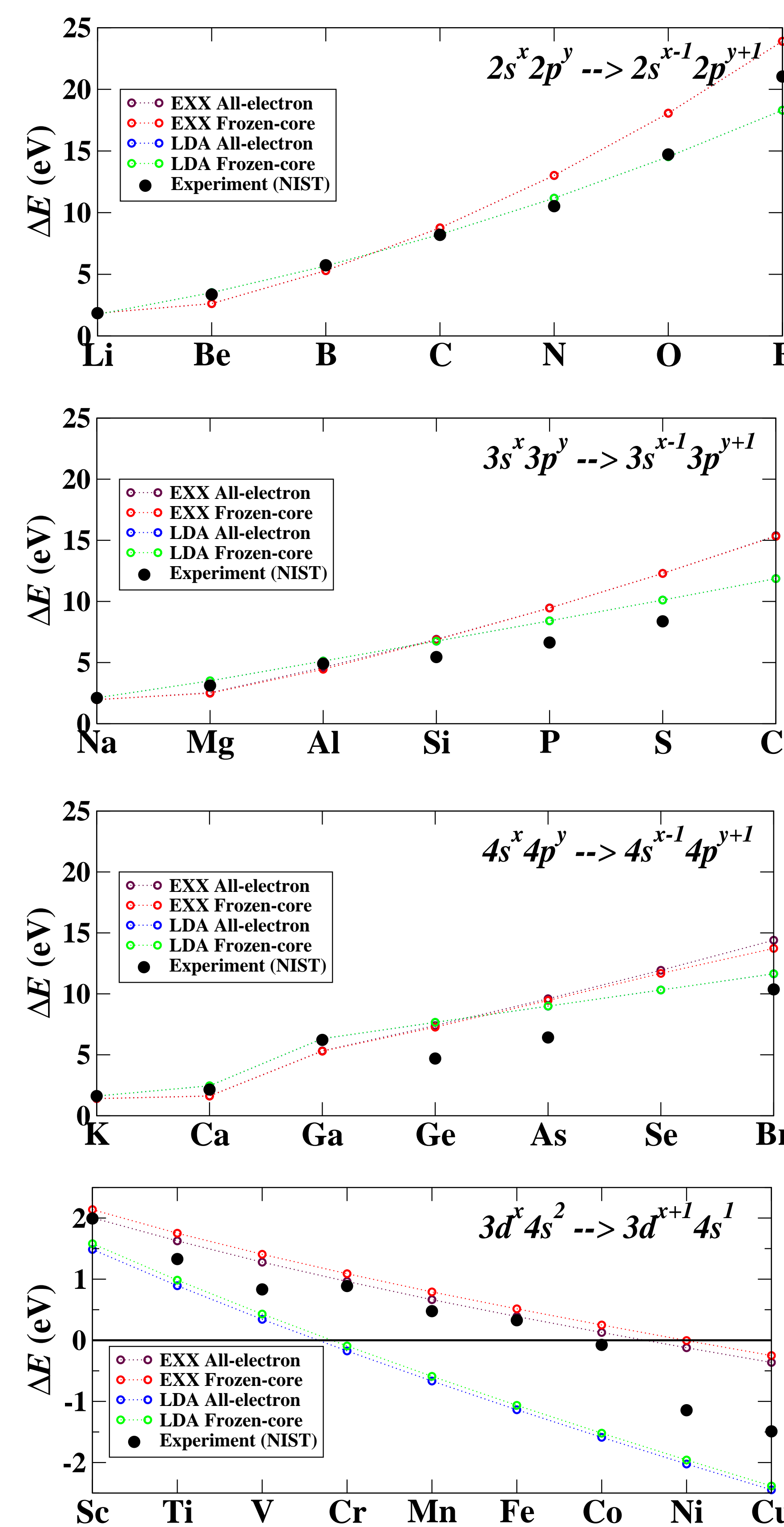


FIG. 3 Plots of energy differences. For the sp materials, the energy differences $\Delta E \equiv E(ns^{x-1}np^{y+1}) - E(ns^x np^y)$ are plotted. For the transition metals, the energy differences $\Delta E \equiv E(4s^{x-1}3d^{y+1}) - E(4s^x 3d^y)$ are plotted. For all of these cases, experimental values of ΔE from NIST⁷ are compared with calculated values including all-electron and frozen-core treatments. In addition to EXX-OEP results, LDA results are included for comparison.

In order to both assess the accuracy of the frozen-core approximation and to compare energy results for the EXX-OEP with the standard local density approximation (LDA), we have studied a series of energy differences across the periodic table as shown in Fig. 3. Since all of the calculations were done for the averaged orbital and spin configurations, the corresponding experimental results should be the average of all of the spectral energy levels of each one-electron configuration. However, in some cases there are missing spectral lines in the data, particularly for the excited states so that the inferred experimental values of ΔE are underestimated.

In general, we find the frozen-core results to be numerically very close to the all electron results, the OEP frozen-core errors being generally larger than those of the LDA, but still within acceptable levels. The frozen-core errors can be considerably reduced by including semi-core states in the set of valence orbitals. The OEP frozen-core errors could perhaps be further reduced by additional refinement of the algorithm. As expected, there are clearly systematic differences in the excitation energies modeled by the LDA and OEP treatments. For the $3d$ transition metal series, the experimental values of ΔE are generally in closer agreement to the OEP results.

PAW-OEP formulation

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

$$H^{\text{PAW}} = \hat{H} + \sum_{aj} |\tilde{p}_i^a\rangle D_{ij}^a \langle \tilde{p}_j^a|, \quad (13)$$

where the pseudo-Hamiltonian \hat{H} contains the pseudo-potential of the form

$$\tilde{V}(\mathbf{r}) = \tilde{V}_{\text{loc}}(\mathbf{r}) + \tilde{V}_H(\mathbf{r}) + \tilde{V}_x^{\text{core}}(\mathbf{r}) + \tilde{V}_x^{\text{vale}}(\mathbf{r}). \quad (14)$$

The effects of core exchange potential $V_x^{\text{core}}(\mathbf{r})$ are represented in the pseudized function $\tilde{V}_x^{\text{core}}(\mathbf{r})$, while $V_x^{\text{vale}}(\mathbf{r})$ represents the pseudized valence exchange potential. The summation in Eq. 13 includes site indices a and basis function indices i, j and the one-center matrix elements D_{ij}^a will also contain contributions from the constant core exchange potentials $V_x^{\text{core}}(\mathbf{r})$ and $V_x^{\text{vale}}(\mathbf{r})$ terms as well as varying contributions from the valence exchange potentials $V_x^{\text{vale}}(\mathbf{r})$ and $V_x^{\text{core}}(\mathbf{r})$. The PAW form of the Kohn-Sham equations (3) for the pseudowavefunctions $\{\tilde{\psi}_n(\mathbf{r})\}$ is

$$(H^{\text{PAW}} - \varepsilon_n O^{\text{PAW}}) \tilde{\psi}_n = 0. \quad (15)$$

Here O^{PAW} denotes the pseudowavefunction orthonormality matrix. The equations for the auxiliary function $\tilde{g}_n(\mathbf{r})$, analogous to Eq. (9) will take the form

$$(H^{\text{PAW}} - \varepsilon_n O^{\text{PAW}}) \tilde{g}_n = \frac{\delta E_x^{\text{PAW}}}{\delta \tilde{\psi}_n^*} - \tilde{V}_x^{\text{vale}} \tilde{\psi}_n - \sum_{aj} \tilde{p}_i^a [V_{c_{ij}}^a \langle \tilde{p}_j^a | \tilde{\psi}_n \rangle - \bar{U}_n \tilde{\psi}_n]. \quad (16)$$

In this expression, only the valence-valence interactions to the PAW exchange functional E_x^{PAW} contribute. The corresponding PAW shift function would then take the form analogous to Eq. (8)

$$\tilde{S}(\mathbf{r}) = -\sum_n \{ \tilde{g}_n^*(\mathbf{r}) \tilde{\psi}_n(\mathbf{r}) + \tilde{g}_n(\mathbf{r}) \tilde{\psi}_n^*(\mathbf{r}) \} \quad (17)$$

for updating $\tilde{V}_x^{\text{vale}}$ and

$$[S_{ij}^a] = -\sum_{aj} \{ \langle \tilde{g}_n | \tilde{p}_i^a \rangle \langle \tilde{p}_j^a | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_n | \tilde{p}_i^a \rangle \langle \tilde{p}_j^a | \tilde{g}_n \rangle \} \quad (18)$$

for updating the one-center matrix elements $[V_{c_{ij}}^a]$.

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Acknowledgements

Supported by NSF grants DMR-0405456, 0427055, and 0705239. Helpful discussion with Leor Kronik are gratefully acknowledged.