

## ARTICLES

**Transferable relativistic Dirac-Slater pseudopotentials**

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We present a method for constructing a scalar-relativistic pseudopotential that provides exact agreement with relativistic Dirac-Slater all-electron eigenvalues at the reference configuration. All-electron wave functions are self-consistently computed in the valence region at the exact all-electron scalar relativistic eigenvalues. This method improves transferability of the resulting pseudopotential and presents a better starting point for the designed nonlocal pseudopotential approach [Phys. Rev. B **59**, 12 471 (1999)]. We present calculations for the gold atom as an example of this approach.

*Ab initio* density functional theory<sup>1,2</sup> (DFT) calculations have been used extensively over the past thirty years to study metals, insulators, and semiconductors. The plane-wave pseudopotential method has been widely used because it is both accurate and fast, enabling calculations on large systems inaccessible with other methods. The pseudopotentials in these calculations mimic the effect of the nuclei and core electrons on the valence electrons, dramatically reducing the computational cost of the calculations. However, poorly constructed pseudopotentials will lead to inaccuracies in the solid-state results. It is desirable that the pseudopotentials be transferable, i.e., that they should be able to mimic the behavior of the all-electron nucleus and core potential in various local environments. The ability of the pseudopotential to reproduce the all-electron valence eigenvalues and total-energy differences of various atomic configurations is extremely important for transferability.<sup>3,4</sup> In addition, pseudopotentials requiring a smaller basis set can significantly speed up solid-state calculations.

Various methods have been developed to accomplish these goals. The *ab initio* pseudopotentials of Hamann, Schlüter and Chiang<sup>5</sup> employ a different spherically symmetric potential for each angular momentum, allowing enforcement of the norm-conservation condition at one atomic configuration, the reference configuration. Norm conservation guarantees exact agreement between the all-electron and pseudopotential eigenvalues and wave functions beyond the core radius  $r_c$  for the reference configuration, and it greatly improves transferability in other configurations. The semilocal norm-conserving pseudopotentials were further developed by Kleinman and Bylander,<sup>6</sup> who transformed the pseudopotential into fully separable nonlocal form, dramatically reducing the memory cost. The optimized pseudopotential method developed by Rappe *et al.*<sup>7</sup> reduces the plane-wave cutoff necessary to use norm-conserving pseudopotentials. The designed nonlocal (DNL) approach of Ramer and Rappe<sup>8</sup> significantly improves the transferability without affecting the convergence properties. Goedecker, Teter, and Hutter<sup>9</sup> have developed highly transferable dual-space

multiple-projector pseudopotentials that are expressed as sums of Gaussians. The Vanderbilt ultrasoft pseudopotential method<sup>10</sup> further lowers the plane-wave cutoff by discarding norm conservation but restoring the correct charge with augmentation charge density functions. In this approach, good transferability is achieved by the use of several projectors. The combination of ultrasoft pseudopotentials with Blöchl's projector-augmented wave<sup>11</sup> method can provide extremely good convergence and transferability. A feature common to all these methods is the preservation of exact agreement of the all-electron and valence eigenvalues at the reference configuration.

Many technologically important materials contain elements with  $Z > 54$ . For such heavy atoms, relativistic effects cannot be ignored without severe consequences for the accuracy of the calculations. The most important change to the Kohn-Sham Hamiltonian is in the kinetic-energy operator. In DFT all-electron atomic calculations the Dirac-Slater and the Koelling-Harmon<sup>12</sup> approaches are widely used. The Dirac-Slater equation includes spin-orbit coupling, producing (for  $s = \frac{1}{2}$ ) a pair of spin-dependent (up and down) wave functions and eigenvalues for every orbital with  $l > 0$ . The Koelling-Harmon approach omits the spin-orbit interaction from the Hamiltonian but retains all other relativistic kinematic effects. Therefore a single "spin-averaged" wave function and eigenvalue are produced for each atomic orbital. This is less accurate than the Dirac-Slater method, but the error thus introduced is often acceptably small. In addition to kinetic and spin-orbit effects, the exact relativistic correction for the local density approximation (LDA) exchange functional is also known but has a small effect on the valence states. Recently, the relativistic exchange functional has been derived within the generalized gradient approximation.<sup>13</sup>

The direct relativistic effects on the valence states of a heavy atom are small. Relativity strongly affects the core states, changing the self-consistent potential seen by the valence orbitals. This implies that a pseudopotential can effectively incorporate relativistic effects in nonrelativistic solid-

state pseudopotential calculations. With a Koelling-Harmon reference atomic all-electron calculation, the pseudopotential construction procedure is not different at all from the nonrelativistic case. However, if a Dirac-Slater all-electron calculation is used as a basis for the pseudopotential construction, there exists a problem of representing the up and down relativistic wave functions and eigenvalues by a single wave function and eigenvalue arising from the nonrelativistic Schrödinger equation. Following the suggestion of Kleinman,<sup>14</sup> Bachelet and Schlüter<sup>15</sup> proposed the construction of separate  $V_{nl}^{\text{up}}(r)$  and  $V_{nl}^{\text{down}}(r)$  for the up and down states. They then create an average pseudopotential weighted by the different  $j$  degeneracies of the  $l \pm \frac{1}{2}$  states:

$$V_{nl}^{\text{AVG}}(r) = \frac{1}{2l+1} [lV_{nl}^{\text{down}}(r) + (l+1)V_{nl}^{\text{up}}(r)]. \quad (1)$$

The Bachelet-Schlüter (BS) averaged pseudopotential contains all scalar parts of the relativistic pseudopotential. This approach gives rise to an error of order  $\alpha^2$ , where  $\alpha$  is the fine structure constant ( $\alpha = \frac{1}{137.04}$ ). However, the eigenvalues of the BS averaged pseudopotential will not be equal to the weighted average of the up and down all-electron eigenvalues. In addition, the valence charge density due to the solutions of the Schrödinger equation for the BS averaged pseudopotential will not be the same as the valence charge density of the all-electron atom. Therefore, exact agreement between the pseudopotential and the all-electron orbital eigenvalues and charge density past  $r_c$  is not preserved even for the reference configuration. Typically, the error in the eigenvalues and total energies introduced by the potential averaging is small, about 1–4 mRy. None of the modern pseudopotential methods can remove this error. Thus, one currently has a choice of either accepting the error due to ignoring the spin-orbit coupling in the all-electron calculations (Koelling-Harmon), or using the more correct Dirac-Slater equations and accepting the error due to pseudopotential averaging. As can be seen from Table I, the error due to the Koelling-Harmon approximation is not negligible and will become more significant as other approximations in DFT calculations such as the exchange-correlation functional are refined.

We present below a method for constructing a pseudopotential whose eigenvalues agree exactly with the averaged relativistic all-electron eigenvalues

$$\epsilon_{nl}^{\text{AVG}} = \frac{1}{2l+1} [l\epsilon_{nl}^{\text{down}} + (l+1)\epsilon_{nl}^{\text{up}}]. \quad (2)$$

It is impossible to enforce charge density agreement with the relativistic all-electron calculation for all  $r > r_c$ , since each wave function decays exponentially and the sum of two exponential functions cannot be equal to a single exponential function at more than two points. Instead, we impose an aggregate norm conservation outside the core radius  $r_c$ . We require the weighted average of the integrals of the squares of the spin-up and spin-down wave functions from  $r_c$  to infinity to be preserved by the new potentials and pseudowave-functions for each valence orbital  $\phi_{nl}$ :

$$Q_{nl} = \int_{r_c}^{\infty} |\phi_{nl}(r)|^2 r^2 dr, \quad (3)$$

$$Q_{nl} = \frac{1}{2l+1} \left( l \int_{r_c}^{\infty} |\psi_{nl}^{\text{down}}(r)|^2 r^2 dr + (l+1) \int_{r_c}^{\infty} |\psi_{nl}^{\text{up}}(r)|^2 r^2 dr \right). \quad (4)$$

Unlike the standard averaging procedure where the spin-up and spin-down *pseudopotentials* are averaged and the averaged pseudopotential is then used to obtain the nonrelativistic wave function and eigenvalues, in our procedure the relativistic all-electron eigenvalues and the aggregate norm-conservation criterion are used to obtain the nonrelativistic wave functions and potentials at the all-electron level.

The algorithm proceeds as follows. First we obtain the relativistic spin-up and spin-down all-electron wave functions and eigenvalues using the Dirac-Slater formalism. The averaged all-electron eigenvalue and norm,  $\epsilon_{nl}^{\text{AVG}}$  and  $Q_{nl}$ , are then computed for each valence orbital. The initial guess for the new nonrelativistic  $\phi_{nl}$  is set to be the weighted average of the spin-up and spin-down Dirac-Slater wave functions  $\psi_{nl}^{\text{up}}$  and  $\psi_{nl}^{\text{down}}$ . The valence charge density  $\rho_{\text{valence}}(r)$  corresponding to  $\phi_{nl}$  is computed and then added to the charge density due to the core orbitals  $\rho_{\text{core}}(r)$  to give total charge density  $\rho_{\text{total}}(r)$ .

The exchange-correlation and Hartree potentials and energy densities are then computed and the full potential  $V(r)$  is obtained. For each orbital the potential  $V(r)$  is used in an inward tail procedure<sup>16</sup> for the new wave function  $\phi_{nl}$  with the criterion  $\epsilon_{nl} = \epsilon_{nl}^{\text{AVG}}$ . Each orbital is scaled so that the norm outside  $r_c$  is equal to  $Q_{nl}$ . For  $r < r_c$ ,  $\phi_{nl}$  is given a smooth nodeless form

$$\phi_{nl}^{\text{AVG}}(r) = r^{l+1} \left[ \frac{\phi_{nl}^{\text{AVG}}(r_c)}{r_c^{l+1}} + c_{nl} \left( 1 - \frac{r}{r_c} \right)^4 \right] \quad (5)$$

with the parameter  $c_{nl}$  chosen such that  $\phi_{nl}$  is normalized to unity. This is done for each valence orbital. The new valence charge density  $\rho_{\text{valence}}(r)$  is then computed from the  $\phi_{nl}$ , completing the cycle. This cycle is repeated until the input and output  $\phi_{nl}$  are equal.

Pseudopotentials are then generated from the converged  $\phi_{nl}$ . The optimized and designed nonlocal pseudopotential methods are used in this paper to improve convergence and transferability. However, we emphasize that the present method of ensuring agreement between relativistic all-electron and pseudopotential results can be used with any pseudopotential generating scheme, such as the ultrasoft construction, since the self-consistent solution is found at the all-electron level.

We have applied our averaging method to the gold atom. Gold has atomic number 79 and therefore must be treated relativistically. We have used a neutral  $6s^{1.0}6p^{0.0}5d^{10.0}$  reference configuration. We use the Perdew-Zunger<sup>17</sup> LDA for the exchange-correlation functional in all calculations.

The results in Table I show that even without DNL construction, our method improves transferability in configurations close to reference, with the sum of absolute values of

TABLE I. Configuration testing for the Bachelet-Schlüter (BS) gold pseudopotential averaging and our all-electron averaging methods described in text. Eigenvalues, eigenvalue errors, and total energy differences are given for all-electron (AE) Dirac-Slater and Koelling-Harmon methods, the BS averaged method, and our all-electron averaged pseudopotential methods with and without the designed nonlocal (DNL) construction. All energies are in Ry.

	AE Dirac-Slater average	AE Koelling-Harmon error	BS averaging error	Present averaging error	BS with DNL error	Present with DNL error
$6s^1$	-0.4457	-0.0018	0.0011	0.0000	0.0011	0.0000
$6p^0$	-0.0696	0.0044	0.0035	0.0000	0.0035	0.0000
$5d^{10}$	-0.5281	0.0050	0.0035	0.0000	0.0035	0.0000
$\Delta E_{\text{tot}}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$6s^2$	-0.5096	-0.0020	0.0013	-0.0002	0.0018	0.0005
$6p^0$	-0.0968	0.0052	0.0050	0.0006	0.0050	0.0004
$5d^9$	-0.6783	0.0051	-0.0027	-0.0051	0.0000	-0.0008
$\Delta E_{\text{tot}}$	0.1246	0.0067	-0.0008	-0.0025	0.0003	-0.0006
$6s^0$	-0.9958	-0.0038	-0.0008	-0.0009	0.0009	-0.0006
$6p^0$	-0.5118	0.0055	0.0038	-0.0036	0.0036	-0.0036
$5d^{10}$	-1.1509	0.0028	0.0037	-0.0010	0.0041	0.0002
$\Delta E_{\text{tot}}$	0.7157	-0.0026	0.0010	-0.0005	0.0010	-0.0004
$6s^1$	-1.0786	-0.0038	0.0010	-0.0014	0.0016	0.0005
$6p^0$	-0.5653	0.0062	0.0059	-0.0025	0.0052	-0.0022
$5d^9$	-1.3211	0.0031	-0.0031	-0.0067	0.0005	-0.0000
$\Delta E_{\text{tot}}$	0.7157	0.0040	0.0010	-0.0033	0.0010	-0.0002
$6s^2$	-1.1611	-0.0039	0.0009	-0.0019	0.0025	0.0013
$6p^0$	-0.6152	0.0070	0.0081	-0.0010	0.0064	-0.0006
$5d^8$	-1.5009	0.0034	-0.0099	-0.0103	-0.0018	-0.0009
$\Delta E_{\text{tot}}$	0.9136	0.0110	0.0004	-0.0103	0.0020	-0.0015
$6s^0$	-1.6971	-0.0049	0.0022	-0.0029	0.0007	0.0015
$6p^0$	-1.0960	0.0067	0.0052	-0.0068	0.0015	-0.0050
$5d^9$	-2.0317	0.0012	-0.0041	-0.0091	0.0001	0.0020
$\Delta E_{\text{tot}}$	1.2040	-0.0003	-0.0071	-0.0054	-0.0008	0.0007
$6s^1$	-1.7974	-0.0058	-0.0018	-0.0040	0.0012	0.0023
$6p^0$	-1.1694	0.0075	0.0074	-0.0050	0.0010	-0.0029
$5d^8$	-2.2275	0.0015	-0.0111	-0.0130	-0.0021	0.0008
$\Delta E_{\text{tot}}$	2.6797	-0.0067	0.0067	-0.0132	0.0012	0.0002
$6s^2$	-1.8947	-0.0059	-0.0015	-0.0042	0.0026	0.0030
$6p^0$	-1.2362	0.0084	0.0100	-0.0024	-0.0010	-0.0008
$5d^7$	-2.4296	0.0017	-0.0154	-0.0115	0.0002	-0.0002
$\Delta E_{\text{tot}}$	3.1615	0.0141	-0.0200	-0.0219	-0.0020	-0.0021

errors in orbital eigenvalues of neutral configurations reduced by 53%. Even more importantly, rigorously correct eigenvalues for the reference configuration enable the designed nonlocal method to improve transferability further. Since the DNL augmentation operator does not affect the pseudo-wave-functions and eigenvalues of the reference configuration, the error given by the pseudopotential averaging method can *never* be corrected with the designed nonlocal

formalism. Furthermore, the augmentation operator has less impact on configurations close to reference than on those further away; thus eigenvalue errors in the neutral configurations are much harder to eliminate for the pseudopotential averaging method than for our all-electron averaging method. While the total transferability error for our all-electron averaging based designed nonlocal potential is 41% less than that of the BS averaging based designed nonlocal

potential, the error in neutral configurations is 89% less. The error in total energy differences summed over all configurations is smaller by 31% for the all-electron averaging method based DNL potential than for the BS averaging procedure based DNL potential.

We have presented in this paper a more accurate method for construction of relativistic pseudopotentials based on Dirac-Slater all-electron atomic calculations. Our procedure enforces the agreement of the pseudopotential and the all-electron spin averaged eigenvalues at the reference configu-

ration, leading to a significant improvement in pseudopotential transferability. The method has negligible computational cost, is easy to implement, and applies to both norm-conserving and ultrasoft pseudopotential formalisms.

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