Transferable relativistic Dirac-Slater pseudopotentials

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We present a method for constructing a scalar-relativistic pseudopotential which 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 non-local pseudopotential approach [Phys. Rev. B 59, 12471 (1999)]. We present calculations for the gold atom as an example of the new approach.

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Ab initio density functional theory (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. The most important indicator of the quality of the pseudopotential is transferability, the ability of the pseudopotential to reproduce the all-electron valence eigenvalues of various atomic configurations. In addition, pseudopotentials requiring a smaller basis set can significantly speed up the solid-state calculation.

Several methods have been developed to accomplish these goals. The ab initio pseudopotentials of Hamann, Schlüter and Chiang employ a different spherically-symmetric potential for each angular momentum, which allows 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 rc for the reference configuration, and it greatly improves transferability in other configurations. The semilocal norm-conserving pseudopotentials were further developed by Kleinman and Bylander who transformed the pseudopotential into fully separable nonlocal form, dramatically reducing the memory cost. The optimized pseudopotential method developed by Rappe et al. reduces the plane-wave cutoff necessary to use norm-conserving pseudopotentials. The designed nonlocal (DNL) approach of Ramer and Rappe significantly improves the transferability without affecting the convergence properties. Goedecker et al. have developed highly transferable dual-space multiple-projector pseudopotentials which are expressed as sums of Gaussians. The Vanderbilt ultrasoft pseudopotential method further lowers the plane-wave cutoff by discarding norm conserva-

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the the pseudopotential construction, there exists a problem of representing the the up and down relativistic wave functions and eigenvalues by a single wave function and eigenvalue arising from the non-relativistic Schrödinger equation. Following the suggestion of Kleinman, Bachelet and Schlüter proposed the construction of separate $V_{nl}^{up}(r)$ and $V_{nl}^{down}(r)$ 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

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

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 ($\alpha = \frac{e^2}{\hbar c m_e}$). 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.

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

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

It is impossible to enforce charge density agreement with the relativistic all-electron calculation for all $r > r_c$, since each wave function asymptotes to an exponential, 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 pseudo-wave functions for each valence orbital $\phi_{nl}$

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

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

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 non-relativistic wave function and eigenvalues, in our procedure the relativistic all-electron eigenvalues and the aggregate norm conservation criterion are used to obtain the non-relativistic 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, $\epsilon_{nl}^{AVG}$ and $Q_{nl}$, are then computed for each valence orbital. The initial guess for the new non-relativistic $\phi_{nl}$ is set to be the weighted average of the spin up and spin down Dirac-Slater wave functions $\psi_{nl}^{up}$ and $\psi_{nl}^{down}$, scaled to preserve $Q_{nl}$. The valence charge density $\rho_{valence}(r)$ corresponding to $\psi_{nl}^{up}$ and $\psi_{nl}^{down}$ is computed and then added to the charge density due to the core orbitals $\rho_{core}(r)$ to give total charge density $\rho_{total}(r)$.

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 solve for the new wave function $\phi_{nl}$ with the criterion $\epsilon_{nl} = \epsilon_{nl}^{AVG}$. 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

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

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 $\rho_{valence}(r)$ 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 insuring 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 solve is done at the all-electron level.

We have applied our new 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 parametrization of the Ceperley-Alder LDA for the exchange-correlation functional in all calculations.

As can be seen from the results in Table I, the new method improves transferability in configurations close to reference, with the sum of absolute values of errors in orbital eigenvalues of neutral configurations reduced by 60%. 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 new all-electron averaging method. While the total transferability error for the new all-electron averaging based designed nonlocal potential is 40% less than that of the BS averaging based designed nonlocal potential, the error in neutral configurations is 78% less.

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 configuration, 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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TABLE I. Configuration testing for the Bachelet-Schlüter (BS) Au pseudopotential averaging and our all-electron averaging methods described in text. Eigenvalues and eigenvalue errors are given for all-electron (AE) weighted average eigenvalues, BS averaged and our all-electron averaged pseudopotential eigenvalues with and without the designed nonlocal (DNL) construction. All energies are in Ry.

|      | AE average | BS averaging | Present BS averaging | with DNL BS average | Present BS averaging with DNL | Present BS average with DNL |
|------|------------|--------------|----------------------|---------------------|-----------------------------|-----------------------------|
| 6s^1 | -0.4457    | 0.0011       | -0.0000              | 0.0011              | 0.0000                      |
| 6p^0 | -0.0696    | 0.0035       | 0.0000               | 0.0035              | 0.0000                      |
| 5d^{10} | -0.5281 | 0.0035       | 0.0000               | 0.0035              | 0.0000                      |
| 6s^2 | -0.5096    | 0.0013       | 0.0001               | 0.0018              | 0.0010                      |
| 6p^0 | -0.0968    | 0.0050       | 0.0006               | 0.0050              | 0.0007                      |
| 5d^9  | -0.6783    | -0.0027      | -0.0064              | 0.0000              | -0.0019                     |
| 6s^0 | -0.9958    | -0.0008      | -0.0013              | 0.0009              | -0.0009                     |
| 6p^0 | -0.5118    | 0.0038       | -0.0037              | 0.0036              | -0.0036                     |
| 5d^{10} | -1.1509 | 0.0037       | -0.0009              | 0.0041              | 0.0006                      |
| 6s^1 | -1.0786    | 0.0010       | -0.0011              | 0.0016              | 0.0007                      |
| 6p^0 | -0.5653    | 0.0059       | -0.0024              | 0.0052              | -0.0018                     |
| 5d^9  | -1.3211    | -0.0031      | -0.0076              | 0.0005              | -0.0009                     |
| 6s^2 | -1.1611    | 0.0009       | -0.0012              | 0.0025              | 0.0023                      |
| 6p^0 | -0.6152    | 0.0081       | -0.0010              | 0.0064              | -0.0003                     |
| 5d^8  | -1.5099    | -0.0099      | -0.0143              | -0.00183             | -0.0022                     |
| 6s^0 | -1.6971    | 0.0022       | -0.0026              | 0.0007              | 0.0001                      |
| 6p^0 | -1.0960    | 0.0052       | -0.0065              | 0.0015              | -0.0055                     |
| 5d^9  | -2.0317    | -0.0041      | -0.0093              | 0.0001              | -0.0001                     |
| 6s^1 | -1.7974    | -0.0018      | -0.0028              | 0.0012              | 0.0015                      |
| 6p^0 | -1.1694    | 0.0074       | -0.0048              | 0.0010              | -0.0030                     |
| 5d^8  | -2.2275    | -0.0111      | -0.0160              | -0.0021             | 0.0013                      |
| 6s^2 | -1.8947    | -0.0015      | -0.0026              | 0.0026              | 0.0033                      |
| 6p^0 | -1.2362    | 0.0100       | -0.0028              | -0.0010             | -0.0002                     |
| 5d^7  | -2.4296    | -0.0154      | -0.0201              | 0.0002              | -0.0001                     |