

Norm-Conserving Pseudopotentials

D. R. Hamann, M. Schlüter, and C. Chiang
Bell Laboratories, Murray Hill, New Jersey 07974
 (Received 1 August 1979)

A very simple procedure to extract pseudopotentials from *ab initio* atomic calculations is presented. The pseudopotentials yield exact eigenvalues and nodeless eigenfunctions which agree with atomic wave functions beyond a chosen radius r_c . Moreover, logarithmic derivatives of real and pseudo wave functions and their first energy derivatives agree for $r > r_c$ guaranteeing excellent transferability of the pseudopotentials.

Pseudopotentials were originally introduced to simplify electronic structure calculations by eliminating the need to include atomic core states and the strong potentials responsible for binding them.¹ Two roughly distinct lines of *recent* development are discernable: In one, ion pseudopotentials of enforced smoothness were empirically fitted to reproduce experimental energy bands.² Consequently, wave functions were only approximately described. In the other, the orthogonalized-plane-wave (OPW) concept underlying the pseudopotential method was used to derive "first principles" pseudopotentials from atomic calculations.^{3,4} These latter potentials are generally "hard core" in character, that is, strongly repulsive at the origin. The resulting wave functions generally exhibit the correct shape outside the core region; however, they differ from the real wave functions by a normalization factor.¹ It is the purpose of this Letter to demonstrate that the normalization and hard-core problems can be solved simultaneously, while also maximizing the range of systems in which a pseudopotential gives accurate results.

The new family of energy-independent pseudopotentials introduced here have the following desirable properties:

- (1) Real and pseudo valence eigenvalues agree for a chosen "prototype" atomic configuration.
- (2) Real and pseudo atomic wave functions agree beyond a chosen "core radius" r_c .
- (3) The integrals from 0 to r of the real and pseudo charge densities agree for $r > r_c$ for each valence state (norm conservation).
- (4) The logarithmic derivatives of the real and pseudo wave function and their *first energy derivatives* agree for $r > r_c$.

Properties (3) and (4) are crucial for the pseudopotential to have optimum *transferability* among a variety of chemical environments in self-consistent calculations in which the pseudo charge density is treated as a real physical object.² This approach stands in contrast to earlier OPW-

like approaches^{1,3,4,5} in which the normalized pseudo wave functions have to be orthogonalized to core states and renormalized in order to yield accurate charge densities outside the core region.⁶ Property (3) guarantees, through Gauss's theorem, that the electrostatic potential produced outside r_c is identical for real and pseudo charge distributions. Property (4) guarantees that the scattering properties of the real ion cores are reproduced *with minimum error* as bonding or banding shifts eigenenergies away from the atomic levels. A central point of our approach is that these two aspects of transferability are related by a simple identity. The method permits the potentials to be intrinsically "soft core" with a continuous range of compromise between potential strength and the "core radius" r_c . Soft-core potentials are advantageous in band-structure calculations employing any kind of Fourier analysis.

The derivation of the identity relating properties (3) and (4) is closely analogous to that of the Friedel sum rule and an identity discussed by Shaw and Harrison⁵ in connection with OPW-like pseudopotentials. We find (in atomic units)

$$2\pi \left[(r\varphi)^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln\varphi \right]_R = 4\pi \int_0^R \varphi^2 r^2 dr. \quad (1)$$

To derive a convenient family of pseudopotentials with properties (1-4), we first carry out an *ab initio* self-consistent full-core atom calculation via a Herman-Skillman-like program,⁷ with use of a local approximation for the exchange and correlation potential. We retain both the potential $V(r)$ and also $u_l(r)$, defined as r times the valence wave function. We choose an analytic cutoff function $f(x)$ which approaches 0 as $x \rightarrow \infty$, approaches 1 at least as fast as x^3 as $x \rightarrow 0$, and cuts off for $x \sim 1$. For each l , we choose a cutoff radius r_{cl} , typically 0.5 to 1.0 times the radius r_{ml} of the outermost peak of u_l . We then form the

potential

$$V_{1l}^{ps}(r) = [1 - f(r/r_{cl})] V(r) + c_l f(r/r_{cl}), \quad (2)$$

which converges to $V(r)$ for $r > r_{cl}$, and adjust the constant c_l so that the nodeless solution w_{1l} of the radial Schrödinger equation with V_{1l}^{ps} has energy ϵ_{1l} equal to the original eigenvalue ϵ_l .

It is clear that property (1) is now satisfied, and that the normalized function w_{1l} satisfies property (2) within a multiplicative constant,

$$\gamma_l w_{1l}(r) \xrightarrow{r > r_c} u_l(r), \quad (3)$$

since both satisfy the same differential equation and homogeneous boundary condition for $r > r_c$.

To satisfy (2)–(4), we now modify the intermediate pseudo wave function w_{1l} to

$$w_{2l}(r) = \gamma_l [w_{1l}(r) + \delta_l g_l(r/r_{cl})], \quad (4)$$

where $g_l(x)$ cuts off to zero for $x > 1$, and behaves as x^{l+1} at small x . The chosen asymptotic behavior of $f(x)$ and $g(x)$ guarantees the potential to be finite at the origin. δ_l is the smaller solution of the quadratic equation resulting from the condition that w_{2l} be normalized,

$$\gamma_l^2 \int_0^\infty [w_{1l}(r) + \delta_l g_l(r/r_{cl})]^2 dr = 1. \quad (5)$$

The final pseudopotential V_{2l}^{ps} producing the nodeless eigenfunction w_{2l} at eigenvalue ϵ_l is now found by inverting the radial Schrödinger equation.

To form the final bare-ion pseudopotential, the valence pseudo charge density is found with use of the w_{2l} wave functions in the same configuration as the original atom calculation. The Coulomb and exchange-correlation potentials due to this density are then calculated and subtracted from each V_{2l}^{ps} . Analytical expressions containing few parameters can subsequently be fitted to the numerical potential functions.⁸

The choice of cutoff functions

$$f(x) = \exp(-x^4), \quad (6)$$

$$g_l(x) = x^{l+1} \exp(-x^4), \quad (7)$$

has provided excellent results in tests on a variety of atoms. Use of the method is illustrated in Fig. 1, in which *s*, *p*, and *d* real and pseudo wave functions are compared for Mo in the configuration $4d^{4.75} 5s^1 5p^{0.25}$. It is clear that each pair of functions converges rapidly for $r > r_{cl}$. The corresponding bare-ion pseudopotential in Fig. 1 is clearly "soft core." It is weak and nearly identical for *s* and *p*, but has a strong attractive *d* well, similar to earlier published pseudopo-

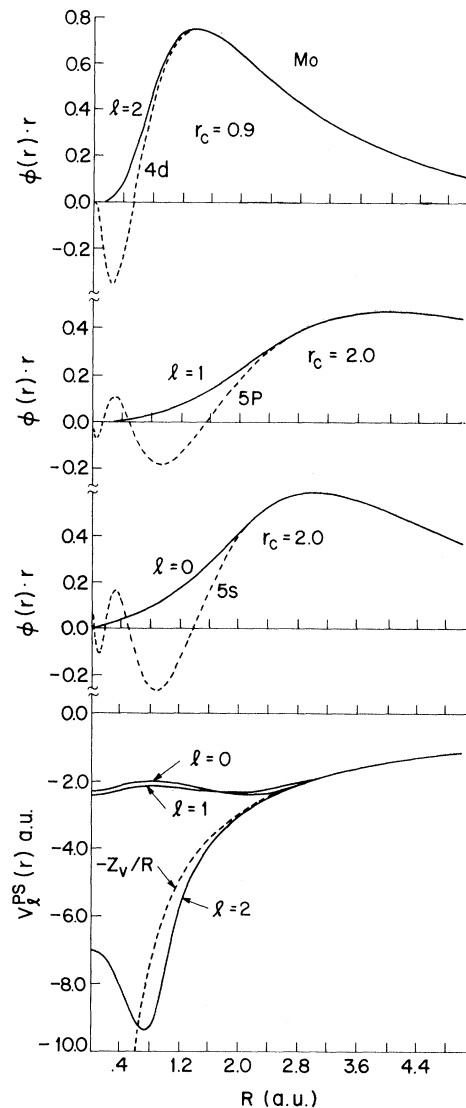


FIG. 1. Comparison of pseudo wave functions (solid lines) and *ab initio* full-core atomic valence wave functions (broken lines) for Mo. The lower panel shows the corresponding bare-ion pseudopotentials.

tentials for the *4d* transition series.¹⁰

Property (4) is illustrated for the Mo atomic pseudopotentials in Fig. 2. The logarithmic derivatives of the real and pseudo wave functions, regular at the origin, are compared at $r = 3$ a.u. for a ± 1 -a.u. energy range straddling the atomic eigenvalues. For $l=2$, the agreement is so good over the entire range that the curves are indistinguishable. For $l=1$, the approach to a core state at -1.38 a.u. produces deviations towards the low-energy end of the range. For positive energies the real and pseudo scattering phase

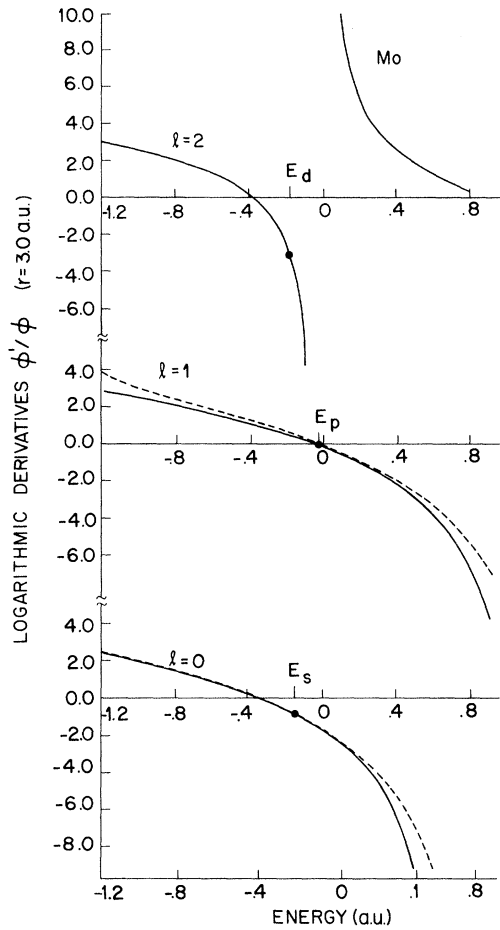


FIG. 2. Energy dependence of logarithmic derivatives at $r=3.0$ a.u. for Mo *ab initio* full-core atomic wave functions (broken lines) and pseudo wave functions (solid lines) as shown in Fig. 1.

shifts must differ as a consequence of Levinson's theorem,¹¹ and the energy scale here is apparently also set by the core binding energies. Band-

structure methods such as augmented plane wave and Korringa-Kohn-Rostoker depend on the lattice potential solely through the logarithmic derivatives at the muffin-tin radius, so that plots such as Fig. 2 give a direct measure of the range over which the pseudopotential will yield accurate bands. Explicit results of band-structure calculations employing these new pseudopotentials will be presented elsewhere.⁸ Tests for bulk Si indicate that real¹² and pseudo charge densities (with $r_c = 0.75r_m$) agree to better than 1%, excluding spheres of radius 1.5 a.u. about each atom. Corresponding band-structure energies agree to better than 0.05 eV over a 20-eV range.

Another test of transferability involving both properties (3) and (4) is given by comparing self-consistent excited configurations of real and pseudo atoms. Such comparisons are shown in Table I for excited, singly and doubly ionized configurations of Mo, Si, and O. The ion-core pseudopotential is that of the ground-state configuration⁹ for which agreement is exact by construction. The excellent agreement of the eigenvalues (i.e., deviations smaller than 0.1 eV over a 30-eV energy range) clearly illustrates the effectiveness of the properties built into these pseudopotentials over a wide region of the periodic table. It should be noted that nodeless wave functions such as the O $2p$ have been constructed by the same procedure, yielding a strongly attractive but nonsingular ion pseudopotential. The pseudopotentials introduced here permit accurate self-consistent calculations, and have the flexibility of a "quality" parameter r_c which can be chosen appropriately for the intended application. The procedure to produce them is exceedingly simple and can be added in the form

TABLE I. Atomic eigenvalues in atomic units for pseudopotentials constructed with $r_{cl} = 0.75r_{m1}$. Δ denotes the deviations from the corresponding full-core *ab initio* results. The Wigner exchange approximation is used.

Configuration	Energy			Δ		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>
O $2s^1 2p^5$	-0.8818	-0.3490	...	-0.0011	-0.0003	...
O $2s^2 2p^3$	-1.4337	-0.8945	...	0.0005	-0.0005	...
O $2s^2 2p^2$	-2.1181	-1.5778	...	-0.0001	-0.0037	...
Si $3s^1 3p^3$	-0.4261	-0.1767	...	-0.0018	0.0001	...
Si $3s^2 3p^1$	-0.6981	-0.4321	...	0.0007	0.0004	...
Si $3s^2 3p^0$	-1.0455	-0.7561	...	0.0031	0.0025	...
Mo $4d^4 5s^1 5p^1$	-0.2108	-0.0865	-0.2740	≈ 0	-0.0006	0.0025
Mo $4d^5 5s^0$	-0.3599	-0.2243	-0.3936	≈ 0	0.0005	-0.0016
Mo $4d^4 5s^0$	-0.6421	-0.4675	-0.7780	-0.0013	-0.0022	-0.0006

of a simple subroutine to any existing local-density atom program.

We have profited from many helpful discussions with G. A. Baraff and V. Heine. One of us (C.C.) is a Bell Laboratories Summer Research Associate.

¹See, M. L. Cohen and V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970) Vol. 24, p. 38, and V. Heine and D. Weaire, *ibid.*, p. 249.

²J. A. Appelbaum and D. R. Hamann, Phys. Rev. B **8**, 1777 (1973); M. Schlüter, J. R. Chelikowsky, S. G. Louie and M. L. Cohen, Phys. Rev. B **12**, 4200 (1975).

³C. F. Melius and W. A. Goddard, III, Phys. Rev. A **10**, 1528 (1974).

⁴A. Zunger and M. L. Cohen, Phys. Rev. Lett. **41**, 53 (1978).

⁵R. W. Shaw and W. A. Harrison, Phys. Rev. **163**, 604 (1967).

⁶Modifications of an OPW-derived pseudopotential to satisfy a similar norm condition starting from a non-local (Hartree-Fock) real potential were recently proposed by A. Redondo, W. A. Goddard, III, and T. C. McGill, Phys. Rev. B **15**, 5038 (1977). These potentials are derived by a basis-function method, and remain singular at $r=0$. Application of this approach to local potentials was later discussed by A. Zunger (to be published).

⁷F. Herman and S. Skillman, in *Atomic Structure Calculation* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

⁸D. R. Hamann and M. Schlüter, to be published.

⁹In order to define a p -like pseudopotential, the Mo atom was excited from its $4d^5 5s^1$ ground-state configuration.

¹⁰See, e.g., S. G. Louie, Phys. Rev. Lett. **40**, 1525 (1978); R. Jacobs, J. Phys. C **1**, 1296 (1968).

¹¹See, L. I. Schiff, *Quantum Mechanics*, (McGraw Hill, New York, 1968) p. 353.

¹²D. R. Hamann, Phys. Rev. Lett. **42**, 662 (1979).