

### Relativistic norm-conserving pseudopotential

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(Received 26 October 1979)

We show that a new pseudopotential recently introduced by Hamann, Schlüter, and Chiang can easily be extended to include all relativistic corrections to order  $\alpha^2$  (not  $Z^2\alpha^2$ ).

Hamann, Schlüter, and Chiang<sup>1</sup> (HSC) recently introduced a new soft-core pseudopotential for which the real and pseudo-atomic wave functions converge identically beyond a chosen core radius  $r_c$ . This is a great advantage over ordinary soft-core pseudopotentials<sup>2,3</sup> where the pseudo-wavefunction differs by a renormalization constant from the real wave function, in that it allows the self-consistent potential to be obtained directly from the pseudo-wavefunctions (the effect of the difference between the pseudo- and real wave functions in the core region is taken account of by the pseudopotential itself). The HSC pseudopotential has the further advantage that it is only very weakly energy dependent. It is the purpose of this comment to point out that the HSC procedure may be applied to the Dirac equation where it leads to a Schrödinger equation containing a weak pseudopotential together with a weak spin-orbit pseudopotential. The eigenfunctions and eigenvalues of this simple Schrödinger equation contain all relativistic corrections to order  $\alpha^2$  (not  $Z^2\alpha^2$ ) and enjoy all the advantages of the nonrelativistic HSC pseudo-wavefunctions.

We write the radial Dirac equations<sup>4</sup> in Hartree atomic units

$$dF/dr - (\kappa/r)F + [\epsilon - V(r)]\alpha G = 0, \quad (1)$$

$$dG/dr + (\kappa/r)G - [2/\alpha^2 + \epsilon - V(r)]\alpha F = 0. \quad (2)$$

Here  $\hbar = m = e = 1$  and  $c = \alpha^{-1} = 137.04$ .  $\epsilon = E - \alpha^{-2}$ , where  $E$  is the relativistic energy. Note that for valence electrons (small  $\epsilon$ ) outside of the core region [small  $V(r)$ ] one may replace  $F$  in Eq. (1) by

$$F = \frac{1}{2} \alpha [dG/dr + (\kappa/r)G] \quad (3)$$

to obtain the Schrödinger equation

$$\frac{1}{2} \left( \frac{d^2G}{dr^2} + \frac{\kappa(\kappa+1)}{r^2} G \right) + [V(r) - \epsilon]G = 0. \quad (4)$$

$r^{-1}G(r)$  is the positive energy radial wave function and  $r^{-1}F(r)$  the negative energy wave function which is strongly admixed with  $G$  in heavy atoms, but only in the core region.  $\kappa$  is a nonzero integer quantum number,

$$\kappa = \begin{cases} J + \frac{1}{2} = l, & \kappa > 0 \\ -(J + \frac{1}{2}) = -(l+1), & \kappa < 0 \end{cases} \quad (5)$$

and the angular wave function associated with  $G(r)$  is<sup>4</sup> (for negative and positive  $\kappa$ , respectively)

$$\Phi_M^J = \left( \frac{l+m+1}{2l+1} \right)^{1/2} Y_l^m(\theta) + \left( \frac{l-m}{2l+1} \right)^{1/2} Y_l^{m+1}(\theta), \quad (6)$$

$$J = l + \frac{1}{2}, \quad M = m + \frac{1}{2}$$

$$\Phi_M^J = \left( \frac{l-m+1}{2l+1} \right)^{1/2} Y_l^{m-1}(\theta) - \left( \frac{l+m}{2l+1} \right)^{1/2} Y_l^m(\theta), \quad (7)$$

$$J = l - \frac{1}{2}, \quad M = m - \frac{1}{2}.$$

For each  $l$  we introduce two preliminary pseudopotentials

$$V_{l\pm 1/2}^{(1)} = [1 - f(r/r_{cl})]V(r) + C_{l\pm 1/2} f(r/r_{cl}), \quad (8)$$

where the cutoff function [ $f(x) \rightarrow 1$  as  $x \rightarrow 0$  and  $f(x) \rightarrow 0$  as  $x \rightarrow \infty$ ] and cutoff radius  $r_{cl}$  are discussed by HSC.  $V(r)$  is the self-consistent potential obtained from a solution of the Dirac equations for the atom.  $C_{l+1/2}$  and  $C_{l-1/2}$  are chosen so that when  $V_{l+1/2}^{(1)}$  and  $V_{l-1/2}^{(1)}$  are inserted in the Schrödinger equation, one obtains nodeless wave functions with eigenvalues equal to those obtained for valence electrons from the Dirac equations with  $\kappa = -(l+1)$  and  $l$ , respectively. To distinguish them from the Dirac eigenfunctions, we will henceforth call the Schrödinger eigenfunctions  $R_{l\pm 1/2}$ . Because  $V_{l\pm 1/2}^{(1)} \rightarrow V(r)$  for  $r > r_{cl}$  and because Eq. (3) is correct to order  $\alpha^2$  [and hence Eq. (4) is equivalent to Eqs. (1) and (2) to order  $\alpha^2$ ], we have, to order  $\alpha^2$ ,

$$\gamma_{l\pm 1/2} R_{l\pm 1/2}^{(1)}(r) = G_{l\pm 1/2}(r), \quad r > r_{cl} \quad (9)$$

where  $\gamma_{l\pm 1/2}$  is a multiplicative constant. Because  $F$  is of order  $\alpha G$  in the valence region, its contribution to the charge density in the valence region may be ignored to order  $\alpha^2$ . Thus following HSC we modify  $R_{l\pm 1/2}^{(1)}$  to

$$R_{l\pm 1/2}^{(2)}(r) = \gamma_{l\pm 1/2} [R_{l\pm 1/2}^{(1)}(r) + \delta_{l\pm 1/2} g_{l\pm 1/2}(r/r_{cl})], \quad (10)$$

where  $g_{l\pm 1/2}(x)$  cuts off to zero for  $x > 1$  and be-

has as  $x^{l+1}$  for small  $x$ .  $\delta_{l\pm 1/2}$  is the smaller solution of the quadratic equation resulting from the normalization condition,<sup>5</sup>  $\int_0^\infty (R_{l\pm 1/2}^{(2)})^2 dr = 1$ . The final pseudopotentials  $V_{l\pm 1/2}^{(2)}$  producing nodeless eigenfunctions  $R_{l\pm 1/2}^{(2)}$  with eigenvalues  $\epsilon_{l\pm 1/2}$  are now found by inverting the nonrelativistic radial Schrödinger equation. The ionic pseudopotentials  $V_{l\pm 1/2}^{\text{ion}}(r)$  are obtained by subtracting from  $V_{l\pm 1/2}^{(2)}$  the Coulomb and exchange-correlation potentials arising from the occupied  $R_{l\pm 1/2}^{(2)}$  states.

Thus the total ionic pseudopotential to be used in an energy band calculation is

$$V_{\text{ps}}^{\text{ion}}(r) = \sum_{l,m} [ |\Phi_M^J\rangle V_{l+1/2}^{\text{ion}}(r) \langle \Phi_M^J| + |\Phi_{M'}^{J'}\rangle V_{l-1/2}^{\text{ion}}(r) \langle \Phi_{M'}^{J'}| ] \quad (11)$$

for  $J = l + \frac{1}{2}$ ,  $M = m + \frac{1}{2}$ ,  $J' = l - \frac{1}{2}$ ,  $M' = m - \frac{1}{2}$ . This may be rewritten

$$V_{\text{ps}}^{\text{ion}}(r) = \sum_l |l\rangle [ V_l^{\text{so}}(r) \vec{L} \cdot \vec{S} + \bar{V}_l^{\text{ion}}(r) + \frac{1}{4} V_l^{\text{so}}(r) ] \langle l|, \quad (12)$$

where

$$V_l^{\text{so}}(r) = \frac{2}{2l+1} [ V_{l+1/2}^{\text{ion}}(r) - V_{l-1/2}^{\text{ion}}(r) ], \quad (13)$$

$$\bar{V}_l^{\text{ion}}(r) = \frac{1}{2} [ V_{l+1/2}^{\text{ion}}(r) + V_{l-1/2}^{\text{ion}}(r) ]. \quad (14)$$

The easiest way to verify that Eq. (12) follows from (11) is to demonstrate<sup>6</sup> that  $\langle \Phi_M^J | V_{\text{ps}}^{\text{ion}}(r) | \Phi_M^J \rangle$  (where  $J = l' \pm \frac{1}{2}$  and  $M = m' \pm \frac{1}{2}$ ) is independent of whether  $V_{\text{ps}}^{\text{ion}}(r)$  is obtained from (11) or (12).

The use of Eq. (12) together with an expansion in plane waves (or perhaps a linear combination of Gaussian orbitals for 5f electrons in the actinides) is a tremendous simplification over other relativistic energy-band calculational techniques, especially if muffin-tin potentials are to be avoided.<sup>7</sup> We wish to emphasize once more that because  $V_{\text{ps}}^{\text{ion}}(r)$  and  $\epsilon$  are of order 1 hartree or less, our procedure is accurate in its inclusion of relativistic effects to order  $\alpha^2$ , i.e., one part in  $10^4$ , whereas most relativistic expansions are accurate to order  $(Z\alpha)^2$ , i.e., about one part in 2 for uranium.

*Note added in proof.* If the Kohn-Sham exchange potential is used, it is the relativistic form [discussed by A. K. Rajagopal, J. Phys. C **11**, L943 (1978)] that must be used in the Dirac equations. Little error is incurred by substituting the nonrelativistic form in the pseudopotential, starting with Eq. (8).

This research was supported by the National Science Foundation under Grant No. DMR 77-21559.

<sup>1</sup>D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

<sup>2</sup>J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

<sup>3</sup>W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

<sup>4</sup>J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics* (McGraw-Hill, New York, 1964).

<sup>5</sup>Equation (4) is correct including terms of order  $\alpha^2$ , whereas neglecting  $F$  in the valence region introduces errors of order  $\alpha^2$  in the charge density. This error is still no larger than that made by neglecting relativistic effects in atomic hydrogen. Even this error can

be eliminated by changing the normalization condition to  $\int_0^\infty [(R_{l\pm 1/2}^{(2)})^2 + (F_{l\pm 1/2}^{(2)})^2] dr = 1$ , where  $F_{l\pm 1/2}^{(2)}$  is obtained from Eq. (3). When the pseudopotential is used in a nonspherical environment, Eq. (3) is replaced by  $F(\vec{r}) = \frac{1}{2} \alpha \vec{\sigma} \cdot \vec{p} R(\vec{r})$ .

<sup>6</sup>Using  $\vec{L} \cdot \vec{S} | \Phi_M^J \rangle = \frac{1}{2} (J^2 - L^2 - S^2) | \Phi_M^J \rangle = \frac{1}{2} [j(j+1) - l(l+1) - \frac{3}{4}] | \Phi_M^J \rangle$ , one easily finds  $\vec{L} \cdot \vec{S} | \Phi_M^J \rangle = \frac{1}{2} l | \Phi_M^J \rangle$  for  $J = l + \frac{1}{2}$ ,  $M = m + \frac{1}{2}$  and  $\vec{L} \cdot \vec{S} | \Phi_M^J \rangle = -\frac{1}{2} (l+1) | \Phi_M^J \rangle$  for  $J = l - \frac{1}{2}$ ,  $M = m - \frac{1}{2}$  and hence proves the equivalence of Eqs. (11) and (12).

<sup>7</sup>N. Elyashar and D. D. Koelling, Phys. Rev. B **15**, 3620 (1977).