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$4f$ resonances with norm-conserving pseudopotentials

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Hamann has shown how to construct a norm-conserving pseudopotential for the unbound $4f$ state in the Ba atom. This pseudopotential which was calculated at -1.877 eV, fails to yield the sharp $4f$ resonance found at $+1.501$ eV in the Dirac atom. We show that this is a consequence not of the energy at which the pseudopotential is calculated but rather of the cutoff radius used. We calculate the pseudopotential at -1.877 eV using a cutoff radius intermediate to those used by Hamann for the bound $4f$ state of the Ba^+ ion and the unbound $4f$ state of Ba, and obtain the positive-energy resonance. When the $[\partial^2(\psi'/\psi)/\partial E^2]$-preserving form of the norm-conserving pseudopotential recently developed by Shirley *et al.* is used, the resonance occurs at 1.507 eV and is actually larger than that of the Dirac atom. We also discuss the application of these new ideas to the separable form of the norm-conserving pseudopotential.

I. INTRODUCTION

Two important advances[1,2] in the theory of pseudopotentials have appeared in print recently. Unoccupied states in atoms such as the $4f$ in Ba are often unbound; the technique for obtaining a pseudopotential for such states has heretofore been to calculate the pseudopotential for the corresponding bound state in the singly ionized atom and to rely on the (approximate) transportability of pseudopotentials from one electronic configuration and energy to another. Hamann[1] showed that it is not necessary to use an eigenfunction to construct the pseudopotential; an unbound wave function normalized within a sphere of radius r_N and calculated at any energy within the range of energies over which the pseudopotential is to be used works just as well. There are only minor constraints on r_N. It must be sufficiently larger than the pseudopotential cutoff radius r_c that the pseudopotential is identical to the true potential at r_N, but not so large that the exponential growth of the unbound wave function causes numerical inaccuracy. In the unusual case that the pseudofunction has one or more nodes,[3] r_N must lie within the first nodal radius. In addition, we have found in the relativistic case that r_N should be sufficiently large that the relative contribution of the small component of the Dirac wave function to the normalization of that function is close to the asymptotically small value it attains as $r_N \to \infty$. Since the potential and eigenvalues in the crystal in which the pseudopotential is to be used are likely to be closer to those of the atom than those of the ion, the Hamann pseudopotential will, in general, be an improvement over the standard pseudopotential for unbound atomic states.

It is well known that pseudopotentials which are norm-conserving[4] generate pseudo-wave-functions which have the same first energy derivative of their logarithmic derivative ψ_l'/ψ_l as the true wave functions and it is this that gives them their transportability over a range of energies. The contribution of Shirley *et al.*[2] (SAMJ) was to show how by parametrizing the cutoff functions used to generate the pseudopotentials one could also force the second energy derivative of the ψ_l'/ψ_l to be equal to those of the true wave functions, thus greatly improving their transportability.

Hamann[1] calculated the Ba $4f$ pseudopotential at the $6s$ eigenvalue $\varepsilon_{6s}=-1.877$ eV using $r_c=2.41$ bohrs, the same r_c he used for the $6s$ pseudopotential. Using this pseudopotential he failed to obtain a set of f bands in BaSe, which he found lie about 9 eV above the top of the valence bands in an all-electron calculation. Hamann states, "of course, when ε_l is deliberately set to avoid a sharp resonance, the pseudopotential cannot be expected to reproduce that resonance." This statement is not quite correct. There is a natural cutoff radius for the $4f$ pseudopotential which will produce the resonance irrespective of ε_l and that r_c is the r_c of the bound $4f$ state in the ion. One is, of course, free to choose any r_c one wants, but the larger r_c is, the less transportable will be the pseudopotential. Hamann's pseudopotential worked well for the valence and lower conduction bands of BaSe not only because it was inherently transportable within that restricted range of energies, but because there is so little f character in those wave functions that any smooth function would have made a satisfactory f pseudopotential. We show in this paper that a pseudopotential generated at Hamann's ε_{6s} with the natural cutoff precisely reproduces the $4f$ resonance of the Dirac equation which lies 3.58 eV above ε_{6s}. It is also transportable to the ion where it results in only a small error in the $4f$ eigenvalue. The disadvantage of this pseudopotential is its slow convergence in reciprocal space so that plane-wave expansions become impossible (except, of course, for states with negligible f character). Therefore we have also generated f pseudopotentials at ε_{6s} with an r_c intermediate to Hamann's and the natural r_c. When $\partial^2(\psi_j'/\psi_f)/\partial E^2$ of the pseudofunction is made to match that of the wave function, the pseudopotential is very nearly as transportable as that with the natural r_c.

Some time ago we[5] introduced a separable form of the norm-conserving pseudopotential which has recently come into very widespread use in molecular-dynamical–density-functional calculations.[6,7] Hamann[1] reported that when he used this form of the pseudopotential, errors between 0.5 and 1.0 eV were obtained in his BaSe energy bands. In the concluding section of this paper we discuss pitfalls to be avoided in constructing the separable form and then show how to extend the ideas SAMJ to separable pseudopotentials obtained from either bound or unbound wave functions in order to make them highly transportable.

II. NORM-CONSERVING f PSEUDOPOTENTIALS

With cutoff radii of 2.405, 1.000, and 0.274 bohr we calculated pseudopotentials for the unbound atomic $4f$ state of Ba at -1.877 eV in exactly the manner of Hamann[1] except that we obtain a $j=\frac{5}{2}$ rather than a spin-orbit averaged pseudopotential and that we used the Vanderbilt[8] form of the pseudopotential cutoff functions. We took $r_M=r_N=3r_c$, where r_M is the radius at which the pseudo and Dirac (large component) ψ_f and ψ_f'/ψ_f are matched, except to avoid complications arising from the small components of the Dirac wave function, for $r_c=0.274$ bohr we took $r_M=r_N=3.000$ bohrs. We did not encounter the difficulty Hamann reported in adjusting the pseudopotential parameter c_l to directly achieve the match[9] of the ψ_l'/ψ_l. (We calculated pseudopotentials for all $l\leq 3$, but found only the f of sufficient interest to report on.) Then using the generalization[10] of Vanderbilt's $f_3(r/r_c)$ given in Eq. (11) of Ref. 2, we constructed $r_c=1.000$- and 2.405-bohr pseudopotentials for which the pseudofunction $\partial^2(\psi_f'/\psi_f)/\partial E^2$ equaled that of the Dirac wave function. For $r_c=0.274$ bohr they were very nearly equal to begin with and no amount of playing with the parameters would bring them any closer. In Fig. 1 the pseudopotentials are displayed. The kink at $r=1.5$ bohrs in the $r_c=1.000$-bohr pseudopotential is not present when the simple Vanderbilt form is used. In Fig. 2 we plot $(K^2/8\pi)V_f(K)$ for the short- and intermediate-range pseudopotentials. We[11] have recently begun employing computational techniques which allow very large plane-wave basis sets to be used in self-consistent energy-band calculations. With these techniques the intermediate-range pseudopotential would be sufficiently convergent in reciprocal space to be used in a BaSe calculation.

We then used these pseudopotentials to calculate the bound $4f$ eigenfunction[12] in Ba$^+$ as well as unbound atomic $4f$ wave functions over a range of positive energies, some of which are displayed in Fig. 3 along with the large component of the Dirac wave functions. These unbound functions are all normalized within a sphere of 29.6 bohrs radius. Such a large radius was chosen so that its exact value relative to the nodes in the various functions would have only a small effect on their relative normalizations. The shape of the resonances seen in the wave functions of Fig. 3 is displayed in Fig. 4, where the height of the resonance peak is plotted as a function of energy. The Dirac and short-range pseudopotential resonances are essentially identical in spite of the fact that the pseudopotential was calculated for an energy 3.58 eV below the resonance. The intermediate-range pseudopotential resonance is actually larger than the Dirac resonance, but has approximately the same shape and loca-

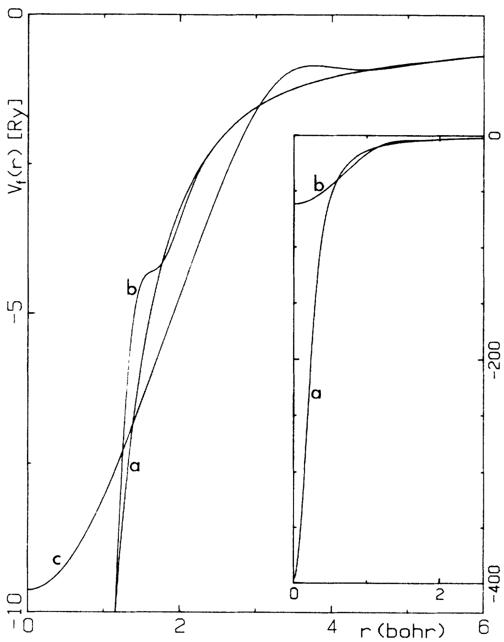

FIG. 1. Ba^{2+} f SAMJ pseudopotentials calculated from unbound atomic states at $\varepsilon=-1.877$ eV with a, $r_c=0.274$ bohr; b, $r_c=1.000$ bohr; c, $r_c=2.405$ bohrs.

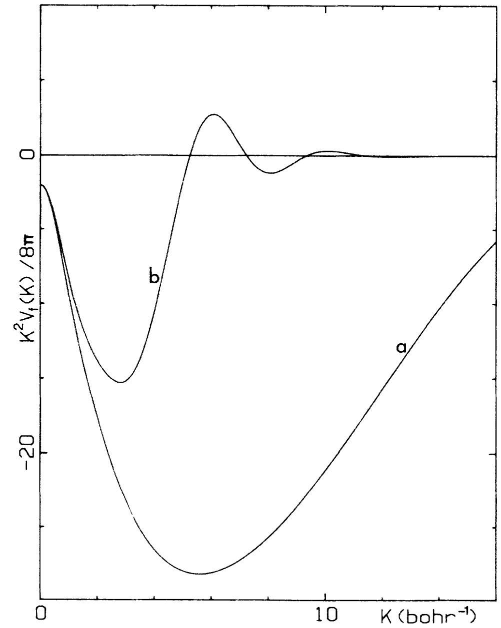

FIG. 2. Plot of the dimensionless quantity $(K^2/8\pi)V_f(K)$ where $V_f(K)$ is the Fourier transform of the $V_f(r)$ of Fig. 1. Note that as $K\rightarrow 0$, $(K^2/8\pi)V(K)\rightarrow Z=-2$.

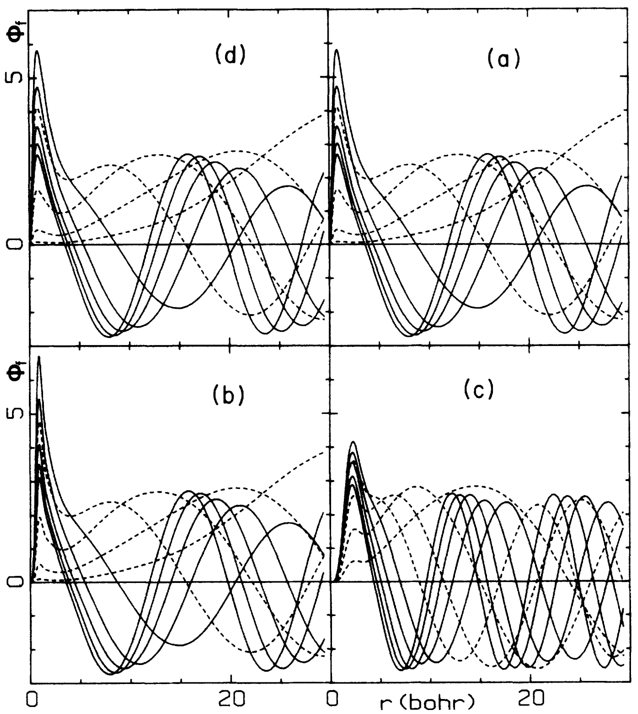

FIG. 3. Plot of Ba f functions $\phi_f = r\psi_f$ (in arbitrary but consistent units) at positive energies. (d) is the large component of the Dirac $j=\frac{5}{2}$ function and (a), (b), and (c) are from the short-, intermediate-, and long-range SAMJ pseudopotentials. The highest peaks are at the resonance energies given in Table I. The other solid (dashed) curves are at energy steps of 0.3 eV above (below) the resonance energy except for (c), where the steps are 0.6 eV.

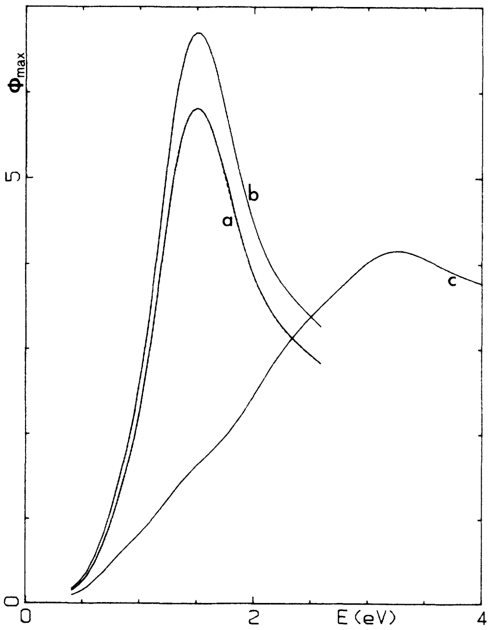

FIG. 4. Maximum value of the first peak in the ϕ_f of Fig. 3 as a function of energy, for a, the short-range pseudopotential; b, the intermediate-range pseudopotential; and c, the long-range pseudopotential. The dashed curve barely visible under curve a is from the Dirac ϕ_f.

tion. The long-range pseudopotential resonance is very broad and occurs at much higher energy.

In Table I are listed the resonance energies, the radius at which the resonant wave functions peak, and the bound-state eigenvalues The first thing worth nothing is that second energy derivative matching of the logarithmic derivatives does give a large improvement in the resonance energies and bound-state eigenvalues for both the intermediate- and long-range pseudopotentials. The second thing to note is that the pseudopotential and Dirac eigenvalues are in much worse agreement than are the resonance energies. SAMJ also suggested a method for adjusting the pseudopotential to make it more transportable to changed potentials. A little thought shows that that would be inappropriate here. The eigenvalue discrepancy does not arise from any shortcoming of the f pseudopotential, rather it arises from the fact that the Dirac and pseudo-6s-eigenfunctions are much different in the core region so that when one of the 6s electrons is removed to form the ion, the Dirac and pseudoatoms experience different potential shifts. Since the s pseudopotential cutoff radius has to lie well beyond the last node in the 6s Dirac eigenfunction, there is really no way to reduce this difference. To see what happens when the same potential shift is applied to the Dirac and pseudoatoms, we calculated the difference between the self-consistent Dirac ionic and atomic potentials and added this to the pseudoatom. We obtained bound 4f states at -4.068 and -4.062 eV for $r_c = 0.274$ and 1.000 bohr, respectively, i.e., the discrepancy between the Dirac and pseudo 4f eigenvalues is no worse than that for the 4f resonances when identical potential shifts are applied to the two atoms to bind the 4f state.

III. SEPARABLE PSEUDOPOTENTIALS

The ordinary norm-conserving pseudopotential is of the form $V_{ps} = \sum_{l,m} |Y_{lm}\rangle V_l(r) \langle Y_{lm}|$. If one uses n plane waves as a basis set, this necessitates the evaluation of $n(n+1)/2$ terms of the form $\int j_l(kr) j_l(k'r) V_l(r) P_l(\cos\theta_{kk'}) r^2\, dr$ at each point in the Brillouin zone, where P_l is a Legendre polynomial of the angle between $\mathbf{k}$ and $\mathbf{k}'$ and j_l is a spherical Bessel function. We[5] therefore suggested writing V_{ps} in the form

$$\hat{V}_{ps} = \sum_{l,m} \frac{|\delta V_l\, \psi^0_{lm}\rangle \langle \psi^0_{lm}\, \delta V_l|}{\langle \psi^0_{lm} | \delta V_l | \psi^0_{lm} \rangle} + V_L(r) , \tag{1}$$

where $V_L(r)$ is a completely arbitrary local potential, ψ^0_{lm} is the pseudoeigenfunction from which V_{ps} was constructed, and $\delta V_l = V_l(r) - V_L(r)$. Note that this reduces the number of nonlocal terms to be evaluated from $n(n+1)/2$ to n. Note also that $\hat{V}_{ps}\psi^0_{lm} \equiv V_{ps}\psi^0_{lm}$, but, in general, $\hat{V}_{ps}\psi \simeq V_{ps}\psi$. There are three criteria that should be observed in selecting a $V_L(r)$. (i) The $\delta V_l(r)$ should be made as small and as short range as possible. (ii) If, as in the present case with our short- or intermediate-range V_f, the V_l are sufficiently dissimilar so that all the δV_l cannot be made small, the positive δV_l should be made small. (iii) The ratios $\langle \psi^0_{lm} | \delta V_l | \psi^0_{lm} \rangle | / \langle \psi^0_{lm} \| \delta V_l \| \psi^0_{lm} \rangle$ should be as close to

TABLE I. The energy of the $4f_{5/2}$ resonance and the radius at which the peak in $\phi_f = r\psi_f$ occurs at resonance for the Ba atom and the energy of the $4f_{5/2}$ bound state for the Ba^+ ion calculated with the Dirac equation and with pseudopotentials with three different cutoff radii. The Ba^{D+} ion is formed by subtracting the potential arising from a Dirac 6s electron from that of the pseudoatom. The first and second columns for the two largest r_c use the Vanderbilt and SAMJ pseudopotentials, respectively.

	Dirac	$r_c = 0.274$ bohr	$r_c = 1.000$ bohr		$r_c = 2.405$ bohrs	
$E_f(\mathrm{Ba})$ (eV)	1.501	1.502	1.607	1.507	4.980	3.253
$R_f(\mathrm{Ba})$ (bohr)	0.83	0.83	0.92	0.92	2.47	2.33
$E_f(\mathrm{Ba}^+)$ (eV)	-4.069	-3.927	-3.827	-3.916	-1.841	-2.365
$E_f(\mathrm{Ba}^{D+})$ (eV)	-4.069	-4.068		-4.062		

unity as possible and in no case less than 0.5. The reasons for these criteria are the following. (i) Since V_{ps} is presumed to be transportable, it is best to keep that part of $\hat{V}_{\mathrm{ps}}$ which differs from V_{ps} as small as possible. (ii) When a very negative V_L is used in the core region resulting in a large positive δV_l, a spurious solution results that has a wave function χ_{lm} which is very large near $r=0$, but also has a node at small r such that $\langle \psi^0_{lm}|\delta V_l|\chi_{lm}\rangle = 0$ but $\int |\chi_{lm}|^2 V_L \, d^3r$ is large and negative. This solution lies well below the real eigenvalues of the pseudopotential. When the sign of V_L and δV_l are reversed, there can be no low-energy spurious solution. (iii) When $\hat{V}_{\mathrm{ps}}$ operates on a crystal pseudo-wave-function ψ_{lm} the ratio $\langle \psi^0_{lm}|\delta V_l|\psi_{lm}\rangle / \langle \psi^0_{lm}|\delta V_l|\psi^0_{lm}\rangle$ multiplies $|\delta V_l \, \psi^0_{lm}\rangle$. Since, in the core region where δV_l is nonvanishing, crystal pseudofunctions are fairly similar to atomic pseudofunctions, this ratio should be close to unity. If $\langle \psi^0_{lm}|\delta V_l|\psi^0_{lm}\rangle$ is small, not because δV_l is inherently small but because δV_l is not of constant sign, the ratio can become quite large, which is obviously unphysical.

Hamann[1] chose $V_L \equiv V_f$. None of his δV_l appear to be large enough to violate the first two criteria, however, his V_f do cross his V_l making his δV_l of unconstant sign and thus very likely violating the third criterion.[13] When he treated the Ba 5p core electrons on an equal footing with the 6s valence electrons, Hamann also violated that part of criterion (i) which says to make δV_l as short range as possible. His 5p pseudopotential cutoff radius is 1.20 bohrs. By using a V_L with a 2.41-bohrs cutoff he extended his δV_{5p} to 2.41 bohrs. Since the 5p pseudopotential is also a good pseudopotential for the 6p states,[14] the uncontrolled change introduced by the long-range V_L cutoff is almost certain to make it much worse for the BaSe valence bands.

We next discuss how δV_l may be changed to insure that $\hat{V}_{\mathrm{ps}}$ yields $\partial^2(\psi'_{lm}/\psi_{lm})/\partial E^2$ identical to those of the Dirac equation. First we note that although $\hat{V}_{\mathrm{ps}}$ is much simpler to use than V_{ps}, when the solution is obtained by expansion in a set of basis functions and matrix diagonalization, it is more tedious when solving the Schrödinger equation numerically. We write

$$-\frac{\partial^2 \phi_{lm}}{\partial r^2} + [V_L(r) - E + g_l(r)]\phi_{lm} = 0 , \tag{2}$$

where $\phi_{lm} = r\psi_{lm}$, $V_L(r)$ here represents the entire local potential, including contributions from the valence-electron-charge density, and

$$g_l(r) = \frac{\langle \psi^0_{lm}|\delta V_l|\psi^{n-1}_{lm}\rangle}{\langle \psi^0_{lm}|\delta V_l|\psi^0_{lm}\rangle} \delta V_l(r)\, \psi^0_{lm}(r) . \tag{3}$$

Because of the nonlocal pseudopotential, the Schrödinger equation must be solved iteratively for ψ_{lm}, and ψ^{n-1}_{lm} in (3) represents the ψ_{lm} of the previous iteration. Both inhomogeneous and homogeneous solutions of (2) must be obtained and $\psi_{lm} = \psi^{\mathrm{homo}}_{lm} + A\psi^{\mathrm{inh}}_{lm}$. In the unbound case A is chosen to normalize ψ_{lm} inside r_N. In the bound case the ψ_{lm} are integrated in from infinity and out from the origin. The A's on either side of the matching point are used to equate the ψ_{lm} and the ψ'_{lm}/ψ_{lm} at the matching point. There is a bound solution for any value of E, but only those E for which the solutions are normalized are eigenvalues.

Although in the atom ψ^0_{lm} and ψ_{lm} are identical when calculated at the same energy, to obtain $\partial^2(\psi'_{lm}/\psi_{lm})/\partial E^2$ we calculate ψ_{lm} at nearby energies using ψ^0_{lm} of the original energy in (3), which results in different second energy derivatives for ψ'_{lm}/ψ_{lm} and $\psi^{0\prime}_{lm}/\psi^0_{lm}$. After selecting a V_L that obeys the stated criteria as well as possible, the procedure is essentially the same for $\hat{V}_{\mathrm{ps}}$ as it was for V_{ps}. The cutoff function is parametrized and the parameters varied [which affects both ψ^0_{lm} and δV_l in (3)] until $\partial^2(\psi'_{lm}/\psi_{lm})/\partial E^2$ is the same as that for the Dirac eigenfunction.

The Ba f pseudopotential—of short enough range to yield the sharp resonance—represents a worse possible case for constructing a separated pseudopotential. We chose $V_L = V_f$ for $r > 1.7$ bohrs and $V_L = V_L(0)[(a-r)/a]^{1/4}$ for $r < 1.7$ bohrs with $V_L(0)$ and a chosen to make V_L and dV_L/dr continuous at $r = 1.7$ bohrs. This makes $\delta V_f = 0$ for $r > 1.7$ bohrs. Although V_f has an r_c of 1.0 bohr, its Vanderbilt cutoff function is still 0.16% of its maximum value at 1.7 bohrs so that δV_f is of no longer range than V_f. We did this for both the Vanderbilt and SAMJ V_f. The latter is displayed in Fig. 5. The separable Vanderbilt pseudopotential resulted in a greater $\partial^2(\psi'_f/\psi_f)/\partial E^2$ error than the nonseparable; the elimination of this error causes the kink in the SAMJ potential in Fig. 5 to be somewhat larger than that in Fig. 1. With some V_L that we tried and discarded the kink became a large oscillation. Note that the kink causes δV_f to have a small positive region. This causes the ratio of criterion (iii) to be 0.9973. We could have chosen $V_L = V_f$ for $r > 1.5$ bohrs which would have made the ratio unity, but which also would have put the kink in V_L

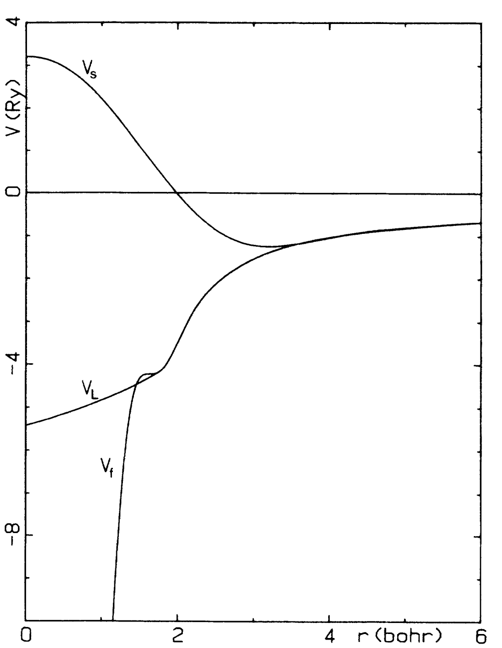

FIG. 5. Ba^{2+} SAMJ s and f separable pseudopotentials together with V_L.

TABLE II. Energy of the $4f_{5/2}$ resonance of the Ba atom and the bound 6s and $4f_{5/2}$ eigenvalues of the Ba^+ ion (formed by subtracting the potential of a Dirac 6s electron from the pseudoatom) calculated from the Dirac equation and using the Vanderbilt and SAMJ separable pseudopotentials. For comparison, the last row lists 6s eigenvalues with nonseparable pseudopotentials.

	Dirac	Vanderbilt	SAMJ
E_f(Ba)	1.501	1.651	1.514
$E_f(Ba^{D+})$	−4.069	−3.932	−4.056
$E_s(Ba^{D+})$	−7.939	−7.936	−7.927
$E_s^N(Ba^{D+})$	−7.939	−7.935	−7.928

and made $V_L(0)$ 1.8 Ry lower, which is getting close to violating criterion (ii).

Using the separable Vanderbilt and SAMJ pseudopotentials we calculated the Ba $4f_{5/2}$ atomic resonance energy (the wave functions are indistinguishable from those in Fig. 3) and the Ba^{D+} $4f_{5/2}$ eigenvalue (where the $D+$ indicates atomic pseudopotential plus the difference between Dirac atomic and ionic valence potentials). The results are listed in Table II. A comparison with the results in the $r_c = 1.000$-bohr column of Table I shows that the separable form of the SAMJ pseudopotential results in negligibly worse results than the local form. Because the results for s electrons depend on the V_L that were chosen to suit the f electrons, we have checked the s eigenvalues for the Ba^{D+} potential. These results are also in Table II, where they are seen to be in excellent agreement with the Dirac eigenvalue. What is surprising is that the Vanderbilt result is better than the SAMJ. We thought this could be a consequence of the fact that their V_L are different (because they were constructed from Vanderbilt and SAMJ f functions) so we also performed the calculations with the nonseparable pseudopotential and, as is seen in Table II, obtained essentially identical results. The removal of a valence electron has two separate effects; it lowers the eigenvalue and it changes the shape of the potential. For the s electron these apparently cause transportability errors of the opposite sign in the pseudopotential and when the former is corrected by making $\partial^2(\psi_s'/\psi_s)/\partial E^2$ agree with the Dirac equation, the total error gets worse. For the f electrons either the errors are of the same sign or, more likely, since the bound f eigenfunctions are of short range compared to the electron that was ionized, the potential shape effects are very small. We note from Eq. (5) of Ref. 2 that if $U(r)$ were constant over the range of the f electrons [where $\lambda U(r)$ is the change in potential], $\partial(\psi_f'/\psi_f)/\partial\lambda$ would be the same for Dirac and norm-conserving pseudo-wave-functions. One could, in principle, make $\partial(\psi_s'/\psi_s)/\partial\lambda$ and $\partial^2(\psi_s'/\psi)/\partial E^2$ both identical to their Dirac values by adjusting parameters in the cutoff function, but we doubt it would be practical to do so.

In conclusion, we have shown that an f pseudopotential calculated from an unbound state at −1.877 eV in the Ba atom yields the Dirac atomic resonance at 1.501 eV and the Ba^{D+} bound state at −4.069 eV with essentially perfect accuracy as long as the cutoff radius is taken to have its natural value $r_c = 0.274$ bohr. When an intermediate cutoff of 1.000 bohr is used, the agreement with the Dirac results is still excellent as long as the SAMJ pseudopotential is used. What is really amazing, however, considering that δV_f is so huge (56.2 Ry at the origin), is that when this pseudopotential is put in the separable form, the error in both the resonance energy and the bound eigenvalue is still only 0.013 eV.

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[9] Hamann fixed c_l and adjusted ε_l to match the ψ'/ψ, then used a perturbational correction to obtain a new c_l and repeated the process until the ε_l that matched the ψ'/ψ was the ε_l at which the Dirac wave function was calculated. We cannot envision any case in which this tedious procedure should be necessary.

[10] We took the parameters $m=\frac{1}{2}$, $n=6$, and varied p as suggested in Ref. 2. For $r_c=0.274$ bohr we also varied m and n.

[11] S. Lee, D. M. Bylander, and L. Kleinman, Phys. Rev. B **40**, 8399 (1989).

[12] We used spin-unpolarized density functionals for the ion since the Dirac equation is not separable when up and down spins see different potentials.

[13] Taking $V_s - V_f = \delta V_s$ for Ba from Fig. 2 of Ref. 1, we see that δV_s is positive for $r < 3.4$ bohrs and very small and negative for $r > 3.4$ bohrs. However, the large r region of the integral is enhanced by the factor of $(r\psi_s^0)^2$ and therefore considerable cancellation exists between the contributions of the two regions to the integral.

[14] The 5p pseudopotential differs from the actual potential over a very small volume compared to the volume filled by the 6p electrons. Also, it correctly forces the 6p pseudofunction to be orthogonal to what is presumably an accurate 5p pseudofunction.