Ghost states for separable, norm-conserving, *ab initio* pseudopotentials

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(Received 16 January 1990)

Some years ago Kleinman and Bylander [Phys. Rev. Lett. **48**, 1425 (1982)] proposed a fully non-local form of norm-conserving pseudopotentials. Its application reduces—if compared to other *ab initio* pseudopotentials—the computational effort to calculate potential matrix elements. However, if the procedure is not applied cautiously, it can destroy important chemical properties of the atoms. In this paper we identify the origin of this problem, and we give a theorem which tells if a "ghost" state occurs below the zero-node state of the atom. We also show how the difficulties can be avoided, i.e., how reliable, fully nonlocal, norm-conserving pseudopotentials can be obtained.

Some years ago Kleinman and Bylander[1] (KB) proposed a fully nonlocal form of norm-conserving pseudopotentials. Its application reduces—if compared to other *ab initio* pseudopotentials—the computational effort to calculate potential matrix elements. Although the suggestion is intriguing, it has not been applied widely. The reason is that the calculated chemical binding of molecules and solids [e.g., GaAs (Ref. 2)] is sometimes described incorrectly. These problems arise, although for atomic calculations the wave functions and the logarithmic derivatives $D_l(E)$ and $dD_l(E)/dE$ at the reference energies E_l and for $r > r_c$ equal those of the all-electron calculations. Here r_c defines the range of "pseudoization" of the ionic potential, and it roughly equals the range of the core electrons.

In this paper we analyze the properties of the KB Hamiltonian and explain why it may cause unphysical results. In short, the problem is due to the fact that the KB Hamiltonian does not obey the Wronskian theorem,[3] which implies that atomic eigenfunctions are energetically ordered such that (for a given quantum number l) the energies increase with the number of nodes. As this theorem is not valid for the KB Hamiltonian, it can have eigenstates with nodes even below the zero-node state. Or, the zero-node states may be followed directly by an $n \geq 2$ node state. Both possibilities will usually prevent an application of these potentials for a reliable description of chemical binding. Below we show how this problem can be avoided, so that no difficulties arise in actual calculations.

We take selenium as an example. In Fig. 1 the highest occupied eigenstates ($4s$ and $4p$) of the all-electron calculation, the corresponding states of the norm-conserving pseudopotential of Bachelet, Hamann, and Schlüter (BHS),[4] and the corresponding results of the BHS-based KB potential are displayed. The two pseudopotential calculations give exactly identical wave functions, which for $r > r_c$ also equal those of the all-electron calculation. Figure 2 shows the logarithmic derivatives of the s, p, and d states of the three calculations. In the d results of the all-electron calculation we also see the Se $3d$ level at -2.01 hartrees, which in the pseudopotential calculations is treated as a core state. We see that at the refer-

ence energies E_l the logarithmic derivatives $D_l(E)$ of the three different calculations are the same, and also the energy derivatives $dD_l(E)/dE$ at E_l are identical. This is a result of the norm-conserving condition. Therefore the
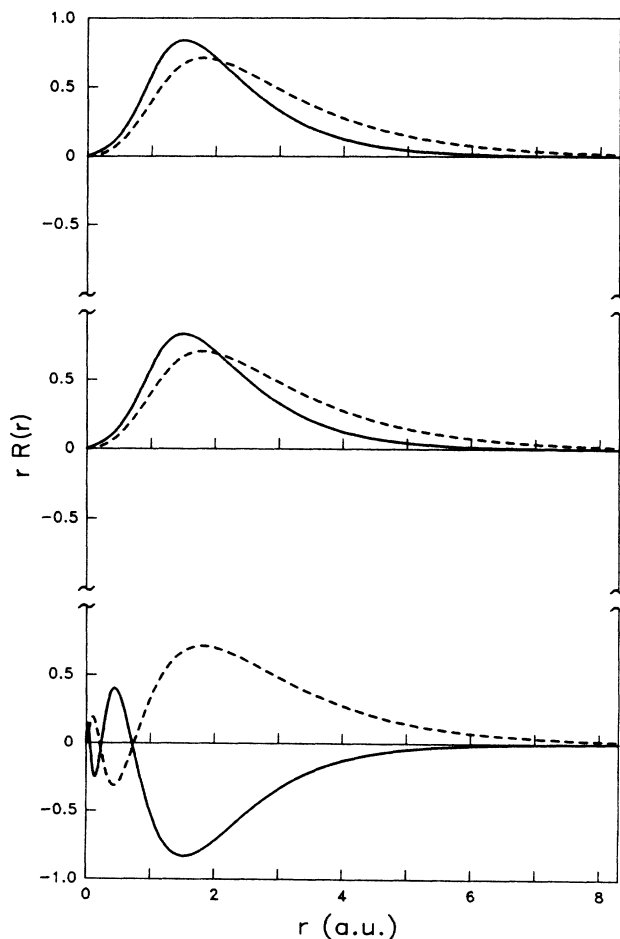

FIG. 1. The $4s$ (solid curve) and $4p$ (dashed curve) wave functions of a Se atom. Bottom: from an all-electron calculation. Middle: from the pseudopotential of Bachelet, Hamann, and Schlüter (Ref. 4). Top: the BHS-based Kleinman-Bylander potential gives the same states as those of the middle row.

scattering of these three potentials is well described in the energy range around E_l. However, for p states the KB potential deviates significantly if we move away from $E_p = -0.24$ hartrees and at -2.94 hartrees we find a "ghost" state (see Fig. 3), i.e., a one-node state below the zero-node reference state. As a consequence, there are also differences in the scattering properties at higher energies.

In order to analyze this problem we note that the "standard" (Hamann-Schlüter-Chiang[5] or Kerker[6]) pseudopotential (ps) of the ion is usually written as an operator,

$$V^{\text{ps-ion}}(\mathbf{r}) = V^{\text{local}}(r) + \sum_{l,m} \Delta V_l(r) |l,m \rangle \langle l,m| . \quad (1)$$

Here $|l,m\rangle$ are normalized spherical harmonics and $\Delta V_l(r)$ is a localized function, which is zero for $r > r_c$. It
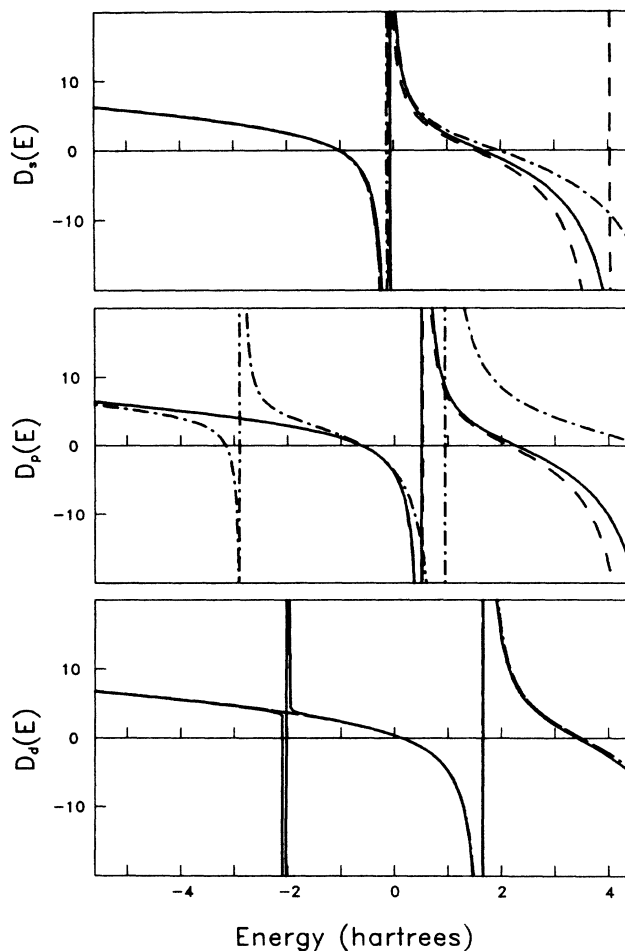

FIG. 2. Logarithmic derivative at $r = 2.33$ a.u. for the s (top), p (middle), and d (bottom) states of a Se atom. Solid curve: results of the all-electron calculation. Dashed curve: results using the potentials of Bachelet, Hamann, and Schlüter (Ref. 4). Dot-dashed curve: results using the BHS-based Kleinman-Bylander potential. At the reference energies $E_s = -0.64$ hartrees, $E_p = -0.24$ hartrees, and $E_d = -0.43$ hartrees the different potentials give the same results. Note that there is an additional p state in the KB potential at $E_{\text{ghost}} = -2.94$ hartrees (also see Fig. 3).
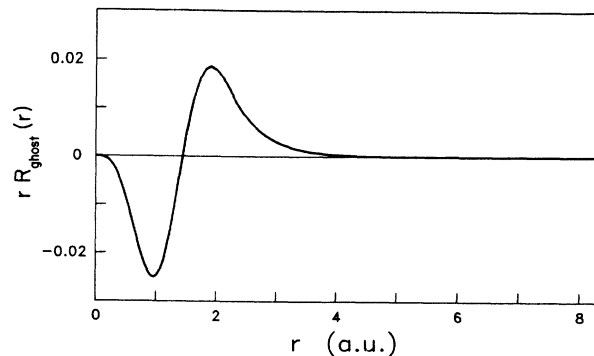

FIG. 3. Radial wave function of the p-like "ghost" state of the BHS-based KB potential.

is often convenient to choose the splitting between V^{local} and ΔV_l such that $\Delta V_l(r)$ vanishes for $l = 2$. For sp-bonded systems the higher-l components of ΔV_l can be neglected. This approximation is acceptable, because all $\Delta V_l(r)$ are localized and for higher-l values the centrifugal potential, $l(l+1)/r^2$, dominates at small values of r. A systematic list of $V^{\text{local}}(r) + \Delta V_l(r)$ for many atoms of the Periodic Table has been compiled by BHS.[4]

Kleinman and Bylander[1] pointed out that a significant reduction of the numerical effort of electronic-structure calculations can be achieved if the nonlocality of the potential is not restricted to the angular parts as in Eq. (1), but if also the radial potential is replaced by a projection operator:

$$\Delta V_l(r) \Longrightarrow E_l^{\text{KB}} |\xi_l \rangle \langle \xi_l| , \quad (2)$$

with

$$\xi_l(r) = \frac{\Delta V_l(r) R_l^{\text{ps}}(r)}{(\langle R_l^{\text{ps}} | \Delta V_l^2 | R_l^{\text{ps}} \rangle)^{1/2}} , \quad (3)$$

which are normalized and well-localized functions (zero for $r > r_c$). The energies E_l^{KB}, which determine the strength of the nonlocality, are given by

$$E_l^{\text{KB}} = \frac{\langle R_l^{\text{ps}} | \Delta V_l^2 | R_l^{\text{ps}} \rangle}{\langle R_l^{\text{ps}} | \Delta V_l | R_l^{\text{ps}} \rangle} . \quad (4)$$

It is obvious that the eigenenergies E_l and the radial wave functions $R_l^{\text{ps}}(r)$ are unchanged by this procedure of Eq. (2): It can be seen immediately that $E_l^{\text{KB}} |\xi_l\rangle \langle \xi_l | R_l^{\text{ps}}(r)$ is identical to $\Delta V_l(r) R_l^{\text{ps}}(r)$.

The possibility that such a fully nonlocal pseudopotential may give rise to a "ghost" prevents a simple application of the BHS potentials. It is important to ensure in the construction of the potentials that no ghost state occurs in the chemically important energy range around E_l. How can one decide if there is a ghost? A careful look at the logarithmic derivatives (compare Fig. 2) may help, but it can be also misleading: A deep-lying ghost state could give rise to a very sharp structure in $D_l(E)$, which then is likely to be missed. Therefore, the following theorem which tells if there is a ghost state below the reference energy level E_l is helpful.

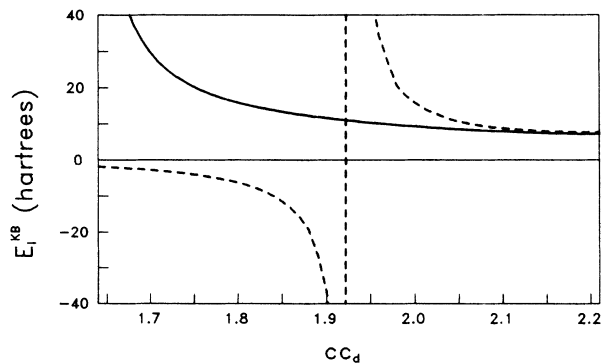It is useful to introduce the "local Hamiltonian,"

FIG. 4. Dependence of the KB energy E_l^{KB} [see Eq. (4)] on the cutoff radius of the Se d pseudopotential (see text). The solid line shows the results for s states and the dashed line those for p states.

which equals the self-consistent nonlocal atomic Hamiltonian without the ΔV_l components. For each l value the two lowest eigenvalues of this local Hamiltonian are $E_l^{local\,0}$ and $E_l^{local\,1}$. As will be shown in detail in Ref. 2, we have to distinguish two possibilities, for which we obtain the following.

(1) $E_l^{KB} < 0$: There is a ghost below the reference level E_l if and only if E_l is higher than $E_l^{local\,0}$ (the energy of the zero-node state of the local Hamiltonian).

(2) $E_l^{KB} > 0$: There is a ghost below the reference level E_l if and only if E_l is higher than $E_l^{local\,1}$ (the energy of the one-node state of the local Hamiltonian).

A detailed proof of this theorem will be given in Ref. 2. For the above-discussed Se BHS potential we obtain $E_s^{KB} > 0$, $E_s = -0.64$ hartrees, and $E_s^{local\,1} = -0.04$ hartrees. Thus, there is no s-like ghost below E_s. For the Se p states the relevant energies are $E_p^{KB} < 0$, $E_p = -0.24$

hartrees, and $E_p^{local\,0} = -0.25$ hartrees. Thus, the above theorem predicts a ghost below E_p, which we indeed had already identified in Figs. 2 and 3.

If we know that there is no ghost below E_l, a careful look at the logarithmic derivative at higher energies is still important. As an example we mention the case of a BHS-based KB pseudopotential for gallium. We do not find a ghost below E_l, but for the s states there is significant deviation of $D_l(E)$ at higher energies (see Ref. 2). As a consequence, the band structure of a calculated GaAs crystal becomes incorrect.

How can one avoid a ghost below E_l and in the chemically important energy range of $E_l \pm 1$ hartrees? As it can be inferred from Eq. (4), the parameter E_l^{KB} depends sensitively on the matrix element $\langle R_l^{ps}|\Delta V_l|R_l^{ps}\rangle$. Analyzing many atoms of the Periodic Table, we found that difficulties and instabilities often occur when this matrix element is close to zero. Then E_l^{KB} is large, and the pseudopotential logarithmic derivative deviates rapidly from the all-electron results if we go away from E_l. Besides
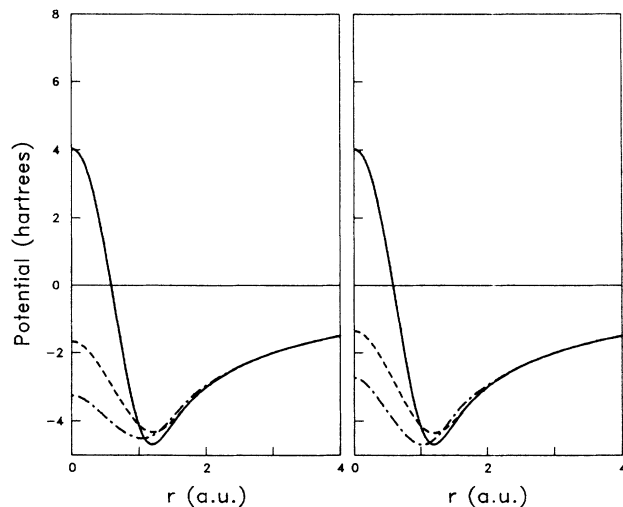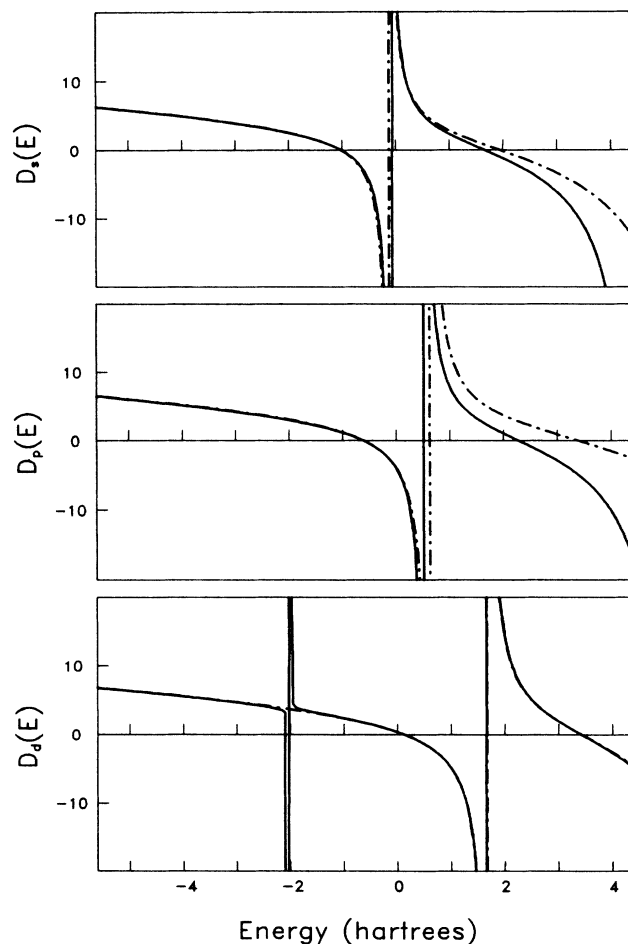

FIG. 5. Left: the Se potential of BHS (Ref. 4) which gives rise to the logarithmic derivatives shown in Fig. 2. Right: our pseudopotential for which no "ghost" state occurs and which gives rise to the logarithmic derivatives in Fig. 6. For the s potential (solid line) and the p potential (dashed line) we start from the ground-state configuration $4s^2 4p^4$. For the d potential (dotted-dashed line) we use $4s^1 4p^{2.75} 4d^{0.25}$.

FIG. 6. Logarithmic derivative at $r = 2.33$ a.u. for the s (top), p (middle), and d (bottom) states of a Se atom. Solid curve: result of the all-electron calculation. Dotted-dashed curve: results using the Kleinman-Bylander procedure based on the potential shown at the right of Fig. 5.

such usually not acceptable inaccuracy, we also noted that self-consistent calculations can become instable. A slight modification of the pseudopotential, which is usually possible without destroying its scattering properties, will significantly change E_l^{KB}. For the Se example this is shown in Fig. 4, where the pseudopotential is modified by changing the cc_l parameter of the d potential. The cc_l parameter is defined[4] by

$$r_c = \frac{r_{max}}{cc_l} , \qquad (5)$$

where r_{max} is the position of the maximum of the radial wave function of the all-electron calculation. We solve the Dirac equation and therefore we obtain different wave functions for s, p spin up, p spin down, d spin up, and d spin down. Therefore our r_c values are different for different l and different spins. For the s- and p-potentials we use $cc_s = 1.6$ and $cc_p = 1.7$. And cc_d is used as the parameter. The l-dependent pseudopotential is then ob-tained from the average of its spin-up and spin-down components. E_l^{KB} is calculated from Eq. (4), using the d pseudopotential as V^{local}. As Fig. 4 shows, the KB energy has a pole at $cc_d = 1.925$. Therefore this cc_d value and values close to it should be avoided. For $cc_d = 2.1$ we obtain a pseudopotential which is very similar to that of BHS,[4] but which does not cause problems in the construction of a fully nonlocal pseudopotential. In Fig. 5 we show the BHS (Ref. 4) and our pseudopotential. Figure 6 displays the logarithmic derivatives, which are now well acceptable for molecular and crystal calculations. At present we perform such analyses for many elements of the Periodic Table. A list of these fully nonlocal, norm-conserving pseudopotentials will be published elsewhere.[7]

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