atomic character is retained even in the bulk because nickel has a significant probability of forming an atomiclike final state with two holes localized on the same atom. Thus we have found a new case in which a property of atomic nickel is manifest in bulk nickel.

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Pseudopotentials in Density-Functional Theory

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The ability of a local pseudopotential to describe accurately core effects in energy calculations is demonstrated. If the pseudopotential is properly chosen, excitation energies of the silicon atom and binding-energy curves of the Si_2 dimer agree well with calculations using the full density functional and the pseudo charge density is virtually identical to the real charge density outside the core region.

Pseudopotential schemes have been used widely in calculations of the electronic properties of semiconductors and their interfaces[1] in order to eliminate numerical difficulties arising from the core electrons and the requirement of orthogonality. The replacement of the core by a local effective potential is, however, an approximation which is difficult to test against *ab initio* calculations, so that questions such as the relationship between the pseudo charge density and the correct charge density are not yet settled. Recently, Wendel and Martin[2] used the density-functional scheme of Hohenberg, Kohn, and Sham[3] to calculate structural energies in silicon using the Si^{4+} pseudopotential of Appelbaum and Hamann.[4] They noted that this potential leads to a substantial underestimate of the lattice constant, necessitating an additional *ad hoc* repulsive force. Since the full density functional reproduces the lattice constants of many bulk materials remarkably accurately,[5] this error is probably a consequence of the pseudopotential approximation rather than the functional scheme itself.

In this Letter, we consider the relation between the full density functional (DF) and the pseudo density functional (PDF). We show that if the pseudopotential is chosen to maximize the similarity between valence orbitals and pseudo orbitals for the Si atomic ground state, a criterion different from that of Appelbaum and Hamann, both schemes give similar results for atomic excitation energies and for binding-energy curves of the Si_2 dimer. In addition, the pseudodensity and the correct density are virtually indistinguishable outside the core region. To our knowledge, this is the first quantitative comparison of energy curves and molecular densities calculated using the density-functional and pseudo-density-functional schemes.

In the DF approach,[3] the total energy of N electrons in the nuclear field $V^{\text{ext}}(\vec{x})$ is obtained by minimizing the functional

$$E[n(\vec{x})]=T_0[n(\vec{x})]+\int d^3x\,n(\vec{x})[\tfrac{1}{2}\varphi(\vec{x})+V^{\text{ext}}(\vec{x})+\epsilon^{\text{xc}}(n(\vec{x}))], \tag{1}$$

where $T_0[n(\vec{x})]$ is the kinetic energy of a noninteracting system with density $n(\vec{x})$ (core plus valence), $\varphi(\vec{x})$ is the Coulomb potential, and $\epsilon^{\text{xc}}(n(\vec{x}))$ is the exchange-correlation energy density, assumed here to have a local form.[6] The PDF scheme used implicitly in Ref. 2 and elsewhere involves replacing the full density in (1) by a pseudodensity obtained from smooth, nodeless valence orbitals, and V^{ext} by a pseudopotential $V_{\text{ps}}{}^{\text{ext}}$ which represents all effects due to core electrons and nuclei. Topiol, Zunger, and Ratner[7] have shown that a strongly l-dependent pseudopotential, obtain from core and valence eigenfunctions of the full density functional for a given atomic reference state, gives eigenvalues and excitation energies of first-row atoms in excellent agreement with the full functional. In contrast to these authors, we choose a local pseudopotential of the form suggested by Starkloff and Joannopoulos,[8] supplemented by a spike at the origin which influences mainly the s function and simulates an l dependence,

$$V_{\text{ps}}{}^{\text{ext}}(r)=\frac{-Z_v}{r}\,\frac{\{1-\exp(-\lambda r)\}}{\{1+\exp(\lambda(r_c-r))\}}+V_0\{\exp[\lambda(r_c-r)]-1\}\theta(r_c-r). \tag{2}$$

Z_v is the atomic valence charge, and the other parameters were chosen to optimize the agreement (for $r>r_c$) between the pseudo eigenfunction and real eigenfunction of the Si-atom ground state. This criterion, also used by Topiol, Zunger, and Ratner,[7] was motivated by our observation[9,10] that dimer binding-energy curves are almost independent of orbital structure in the core region, but very sensitive to tail behavior. Acceptable tails result only for large λ, so that (2) resembles an Ashcroft potential[11] and rapidly attains the correct asymptotic value $-Z_v/r$. The tails corresponding to $\lambda=14$ a.u., $r_c=0.98$ a.u., and $V_0=0.2$ Ry are shown in Fig. 1. Remarkably, tail agreement is almost as good for excited states and for Si$^+$, indicating that this form of potential is only weakly energy dependent. This is because r_c and V_0 are determined by the positions of the final nodes in the $3s, 3p$ eigenfunctions which are fixed in turn by the core functions.

The accurate fit to the tails and the correct form of the core potential outside the core region mean that the eigenvalues, ϵ_i, of the pseudopotential and full potential are approximately equal, as shown in Table I, where we also give excitation energies for the $3s^1 3p^3$ and $3s^2 3p^1$ configurations. It is not obvious that the energy differences should agree since each term in (1) is quite different in the DF and PDF cases. However, both functionals satisfy $\partial E(n)/\partial n_i=\epsilon_i[n_i]$, where n_i is an occupation number,[12] so that the error in the ionization potential, for instance, is

$$\delta I_p=\int_0^1 dn_i[\epsilon_p{}^{\text{ps}}(s^2 3p^{2-n_i})-\epsilon_{3p}(3s^2 3p^{2-n_i})], \tag{3}$$

and cannot exceed the errors in the eigenvalues. This argument assumes that the pseudo density functional has a *fixed* core potential and it shows that introducing configuration-dependent pseudopotentials to reproduce, for example, the exact eigenvalues would not lead to improvement since (3) no longer holds. Although eigenvalues for a given reference state can be fitted with essentially any pseudopotential form, our choice, which has the correct asymptotic behavior and gives optimal tails for the ground state, maximizes the range of configurations over which $\epsilon_i{}^{\text{ps}}\sim\epsilon_i$.

The above results show that the balance in

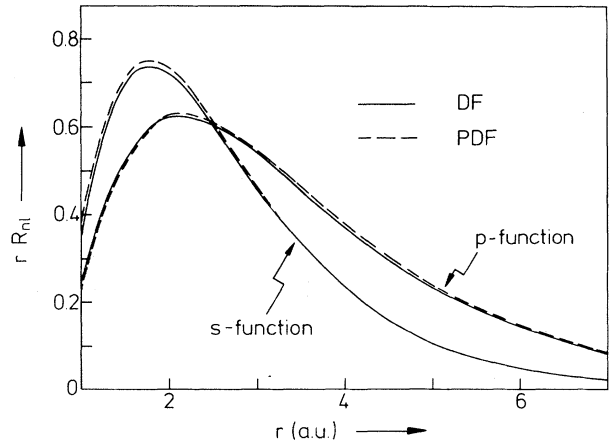

FIG. 1. Tails of valence eigenfunctions for the Si atom calculated with use of the full density function (DF, full curve) and the pseudopotential of Eq. (2) (PDF, broken curve).

TABLE I. Eigenvalues ϵ_i and energy differences ΔE for the Si atom (in rydbergs). Values with superscript from pseudo density functional; others from full functional.

	Si($3s^2 3p^2$)	Si($3s^1 3p^3$)	Si$^+$($3s^2 3p$)
ϵ_{3p}	−0.321	−0.363	−0.882
ϵ_p^{ps}	−0.321	−0.365	−0.871
ϵ_{3s}	−0.813	−0.867	−1.420
ϵ_s^{ps}	−0.828	−0.885	−1.427
ΔE	...	0.293	0.627
ΔE^{ps}	...	0.281	0.625

kinetic and potential energy changes when an electron enters the Si core is approximated well by a properly chosen pseudopotential and support use of the pseudo functional in other contexts.

In order to test the application of the PDF approach to chemical bonding, we have calculated the binding-energy curves of the silicon dimer and compared the results with our recent density-functional calculations.[9] Minimization of the functionals is achieved by solving a differential equation and, since the approximations made are identical in the two cases, any basis errors are the same. In Fig. 2, we compare curve *a* the DF result with curve *b* that obtained using (2) with the above parameters. The agreement is very good and similar results are found for other states of the molecule. All show small but increasing erros at smaller internuclear separations, which may be due to the core relaxation present in the full calculation or to the small deviations in the orbital tails shown in Fig. 1. With this choice of pseudopotential, the pseudo and real molecular densities outside the core region are virtually indistinguishable. Curve *c* also corresponds to (2), but with $r_c = 1.07$, $\lambda = 12.0$, and $V_0 = 0$. In this case, the *s* tail is fitted very well, but the *p* tail is displaced outwards by about 0.1 a.u. This small change produces a pronounced increase in the energy at small separations due to increased core penetration by the *p* tails. In fact, curve *c* agrees well with DF results for the ground state of Ge_2, which is further evidence in favor of the similarity criterion since tails obtained with these parameters fit the correct tails of Ge better than those of Si.[10]

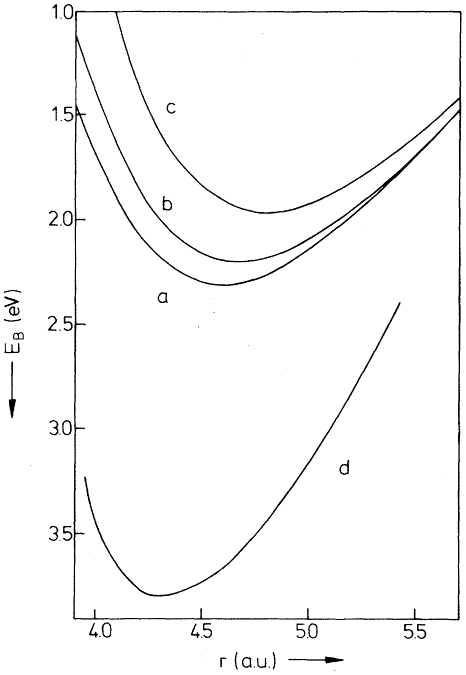

FIG. 2. Binding-energy curves for the ground state of Si_2: curve *a*, density functional; curve *b*, PDF [Eq. (2)] with $\lambda = 14$ a.u., $r_c = 0.98$ a.u., $V_0 = 0.2$ Ry; curve *c*, PDF [Eq. (2)] with $\lambda = 12$ a.u., $r_c = 1.07$ a.u., $V_0 = 0$; curve *d*, PDF with core potential of Ref. 4.

Curve *d* in Fig. 2 results from using the pseudopotential of Ref. 4, which is quite different from (2) and, in particular, is significantly more attractive than $-Z_v/r$ outside the core region. The tails then fall off too rapidly and the reduced core penetration results in an increased binding energy in the dimer. This potential was constructed using $X\alpha$ screening and fitting calculated band gaps for bulk silicon to optical data. To demonstrate that $X\alpha$ screening is not responsible for the discrepancy, we have repeated atom and molecule calculations using this approximation for $\epsilon^{xc}(n)$ with $\alpha = 0.76$. This disagreement in the tails is almost identical and the binding-energy curve shows the same shift from the full density function (with $X\alpha$) as evident in Fig. 2. Whether $X\alpha$ or local density screening is used, this potential also gives an ionization energy for the Si atom larger than the DF result by 7%.

Although the lowest curve in Fig. 2 gives a binding energy which is in better agreement with experiment than the others, this is due largely to the "common-κ" linear muffin-tin orbital basis we use[13] which leads consistently to underestimates of the binding energy and vibration frequency and overestimates of the equilibrium separation. Since the basis errors are the same for all curves, an exact solution of the one-electron equations would move the upper curves towards the experimental binding energy (3.2 ± 0.2 eV) and the curve using the Appelbaum-Hamann core potential away from experiment. An overestimate of binding energy and an underestimate of the equilibrium separation would be consistent with the experience of Wendel and Martin[2] in using this potential for bulk silicon.

The present results demonstrate that the pseudo density functional can give an excellent approximation to the full density functional in molecular as well as atomic geometries and provide strong support for its use in energy calculations in bulk and surface problems. The binding-energy curves are, however, extremely sensitive to the choice of pseudopotential, which should therefore be chosen with care and according to the criterion mentioned above. Since the nearest-neighbor distance in bulk silicon is approximately 5% greater than in the dimer, a somewhat reduced sensitivity may arise in the bulk calculations provided the tails have the correct asymptotic form.

Although the present results are for silicon, the same correspondence between the pseudo and real functionals should hold in general. Starkloff and Joannopoulos[8] have been able to describe atomic tails reasonably well for a wide variety of atoms and even better agreement should be possible by using additional pseudopotential parameters.

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Magnetic Reduction of Photothreshold in Doped EuO

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Reduction of the photothreshold in degenerately doped EuO below the Curie temperature is shown to arise from a magnetically induced space charge layer at the surface. A good fit to the measured shift versus temperature for EuO–2% La is obtained within a simple model, yielding new information about the magnetic nature of the semiconductor surface.

Recent measurement of the total photoelectric yield from the nearly ideal Heisenberg ferromagnet, EuO, degenerately doped with trivalent La, shows a marked reduction of the photothreshold when the sample orders magnetically, whereas for pure samples, no photothreshold shift is recorded.[1,2] Similar shifts are obtained with Gd-doped EuO, indicating that the magnetic nature of the donor is unimportant.

The emission is primarily from the localized $4f$ states of Eu^{++}, which lie in the semiconductor gap, and from the wide $2p$ valence band of O^{--}. The photocurrent stemming from the degenerately doped $5d$ conduction bands is too small to be observed. Since the threshold shift appears to be independent of the spatial distribution or spin polarization of the initial state, core-level relaxation or final-state interactions are an unlikely