Density-Functional Pseudopotential Approach to Crystal Phase Stability and Electronic Structure

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We show that a first-principles nonlocal pseudopotential theory, based on an all-electron density-functional formalism, provides an essentially exact topological separation of both the octet A^NB^{8-N} structures and the suboctet A^NB^{P-N} ($3 \leq P \leq 6$) structures for 77 and 56 non–transition-metal compounds, respectively. These pseudopotentials which also yield accurate descriptions of atomic and bulk solid electronic structure have been computed for 68 transition and nontransition elements.

It is possible to describe[1] the one-electron valence properties of a large number of systems with model nonlocal pseudopotentials truncated at wave vectors $q_t \lesssim 3k_F$, where k_F is the Fermi momentum. However, Simons,[2] Simons and Bloch[3] (SB), and St. John and Bloch[4] have observed that a nonlocal pseudopotential with high-momentum components originating from a strongly repulsive core could yield information on phase stabilities and crystal structures. The Simons-Bloch potential, V_{SB}, is a nonlocal pseudopotential with parameters determined from the observed spectra of hydrogenlike stripped ions. The classical turning points of V_{SB} for angular momentum l, r_l, are useful structural indices capable of separating crystal phases of the octet A^NB^{8-N} compounds,[4] and the suboctet A^NB^{P-N} ($3 \leq P \leq 6$) compounds.[5] Recently Chelikowsky and Phillips[6] have shown that the r_l can also be used to reproduce the parameters of the phenomenological thermochemical scale of Miedema, de Boer, and de Chatel.[7] While the empirical SB approach concentrates on the high-momentum parts of the potential which are responsible for the formation in real space of the structurally significant turning points, this approach is only qualitatively successful in electronic structure studies[8,9] which depend on smaller-momentum-transfer scattering events.

We introduce a first-principles parameter-free pseudopotential (V_{FP}) based on the density-functional formalism, capable of giving an accurate description of the energy spectrum and wave functions of ions, atoms, and solids as well as providing accurate structural information through turning-point radii. We show that the empirical SB potential corresponds to a limiting form of V_{FP} and additional terms V_{FP} make it also suitable for the description of electronic structure. The nonempirical nature of this approach allows interpretation of the r_l in terms of the microscopic constructs of the potential such as Coulomb and exchange-correlation orthogonality holes, core-valence interaction, screening, and orthogonality cancellation. These potentials have been used to analyze the structure of 77 octet and 56 suboctet compounds yielding a structural phase separation that is at least as good as, and in some cases better than, that obtained with the empirical SB scale. Further, application to self-consistent band calculations of Si, Ge, and Mo and to the calculation of atomic excitation energies (obtained as total-energy differences) and wave-function moments yield excellent results compared with the all-electron results.

We assume knowledge of the solutions $\{\psi_{nl}, \epsilon_{nl}\}$ of the ground-state all-electron density-functional equations for the neutral atom, characterized by the potential $V_{tot}[\rho(r)]$ and density $\rho(r)$. Here $V_{tot}[\rho(r)]$ includes the electron-nuclear $-(Z_c+Z_v)/r$, Coulomb electron-electron $V_{ee}[\rho(r)]$, and exchange-correlation $V_{xc}[\rho(r)]$ potentials, where $\rho(r) = \rho^c(r) + \rho^v(r)$ includes the all-electron core (c) and valence (v) charge density. We then determine a potential $V_l(r)$ variationally to solve the equivalent problem in the valence subspace,[10]

$$\{-\tfrac{1}{2}\nabla^2 + V_l(r) + V_{tot}[n^v(r)]\}\chi_{nl}(r) = \epsilon_{nl}{}^v\chi_{nl}(r), \quad (1)$$

such that $\epsilon_{nl}{}^v$ be equal to the all-electron valence spectrum ϵ_{nl} in the reference ground-state configuration and the pseudo wave functions $\chi_{nl}(r)$ be related to the all-electron core-plus-valence solutions $\psi_{n'l}(r)$ by an l dependent unitary rotation with coefficients $C_{n,n'}{}^{(l)}$. Here $n^v(r)$ denotes the variational valence pseudocharge density obtained from Eq. (1). The transformation coefficients $C_{n,n'}{}^{(l)}$ are determined by requiring that there be maximum similarity between χ and ψ[10,11] with elimination of all radial nodes in χ and minimization of its radial kinetic energy. This results in pseudo wave functions that accurately reproduce the all-electron results in the chemically significant bond region[10] and fixes the nonlocal core potential $V_{FP}^{(l)}(r) = V_l(r) - Z_v/r + l(l+1)/r^2$ as

$$V_{FP}^{(l)}(r) = \{U_l(r) + l(l+1)/2r^2\} - Z_v/r + V_{tot}[\rho^c] + \{V_{xc}[\rho^c+\rho^v] - V_{xc}[\rho^c] - V_{xc}[\rho^v]\} + \{V_{ee}[\rho^v] - V_{ee}[n^v]\} + \{V_{xc}[\rho^v] - V_{xc}[n^v]\}, \quad (2)$$

where the repulsive potential $U_l(r)$ is given by

$$U_l(r) = \frac{\sum_{n'} C_{n,n'}^{(l)}(\epsilon_{nl}^{\ v} - \epsilon_{n'l})\psi_{n'l}}{\sum_{n'} C_{n,n'}^{(l)}\psi_{n'l}}. \quad (3)$$

The first term in the curly brackets contains the nonlocality while the rest of the terms represent the local pseudopotential. This potential has a simple physical interpretation. The Pauli term $U_l(r)$ acts to replace the core-valence orthogonality constraints which have been removed in the pseudopotential representation; when there are no core states with angular-momentum symmetry l, one obtains $C_{n,n'}^{(l)} = \delta_{n,n'}$ and $U_l(r) \equiv 0$. Otherwise, $U_l(r)$ is strongly repulsive with a limiting form C_l/r^2 at small r (representing a positive effective centrifugal barrier, replacing the orthogonality constraint). This tends to partially cancel the Coulomb attraction $-Z_v/r$. This behavior is a property of $\chi_{nl}(r)$ alone when it is represented as a combination of all $\psi_{nl}(r)$ subject to a maximum-similarity constraint. The degree of cancellation emerges naturally from the physically appealing maximum-similarity constraint imposed on the wave functions. The third term in (2) represents the screened potential of a neutral core, while the fourth term measures the nonlinearity of the exchange-correlation interactions with respect to the interfering core and valence densities. The last two terms are, respectively, the Coulomb and exchange-correlation orthogonality hole potentials and emerge from the corresponding interelectronic interactions in the regions of space where a pseudopotential charge-density depletion has occurred.

The classical turning points of (2) represent the position where the Pauli potential is just balanced by the Coulomb attraction, renormalized by the core-valence interactions and the orthogonality hole effects. Different choices of $\chi_{nl}(r)$ leading to an overall maximum similarity to $\chi_{nl}(r)$ are found to produce very similar r_l^0 values (but possibly different C_l values). The empirical SB form[2-4] can be identified as the first two terms in (2) where the Pauli term $U_l(r)$ is replaced by its limiting form at small r with an adjustable parameter B_l: $U_l \sim B_l/r^2$. This strongly underestimates the radii for l present in the core and leads to poor wave functions[8,9] because of the unphysically long range of B_l/r^2 and the implicit use of highly relaxed stripped-ion orbitals instead of the more appropriate ground-state wave functions.

We have solved (1) self-consistently for excited atomic and ionic states of 68 transition and nontransition elements, spanning in each case a wide range of electronic configurations and orbital delocalization.[12] We find that the results match the all-electron eigenvalues, total-energy differences, and orbital moments $\langle r_{nl}^{\ \lambda}\rangle$ for $\lambda = -1$, 1, 2, and 3 with an accuracy better than 0.03 eV, 0.05 eV, and 2–3%, respectively, over an excitation energy range comparable to the bandwidth of the corresponding solid. We conclude that $V_{FP}^{(l)}(r)$ is only weakly energy (or state) dependent and can be used to study atoms in solids, in a wide range of bonding configurations. To assure that the values of the radii are unaffected by the particular fashion the orbitals are assigned to core and valence, we screen $F_{FP}^{(l)}(r)$ self-consistently and numerically determine the turning points of the effective potential in (1).

Following St. John and Bloch,[4] for each binary AB compound we construct the structural coordinates $R_\pi = (r_p^{\ A} - r_s^{\ A}) + (r_p^{\ B} - r_s^{\ B})$ and $R_\sigma = (r_p^{\ A} + r_s^{\ A}) - (r_p^{\ B} + r_s^{\ B})$. These are used to construct topological R_π vs R_σ maps for 77 octet (Fig. 1) and 56 suboctet (Fig. 2) compounds. We see that these coordinates separate all the crystal phases very accurately, including the most "sensitive" pairs such as zinc-blende–wurtzite and diamond-graphite and that the same scale applies equally well to electronically compensated A^NB^{8-N} and uncompensated A^NB^{P-N} ($3 \leq P \leq 6$) compounds. This is the first successful phase separation of both octet and suboctet compounds obtained within a nonempirical first-principles model.

Among the notable exceptions we note that CuF appears here and in the SB scheme[13] near the wurtzite-rocksalt line, while it was thought to crystalize in a zinc-blende form. A recent reexamination of the data[13] has suggested that in fact this compound does not exist in its stable phase as an AB compound. The general quality of the separation is similar to that obtained with the empirical SB scheme[4,13]; however a few notable differences occur in which the present results

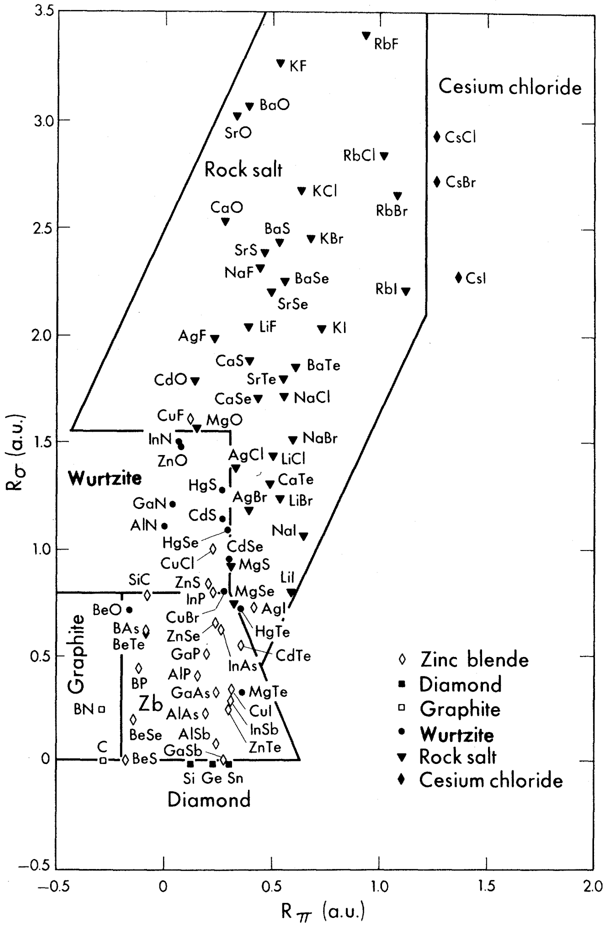

FIG. 1. R_σ vs R_π plot for the octet binary compounds. The separation lines are included for convenience.

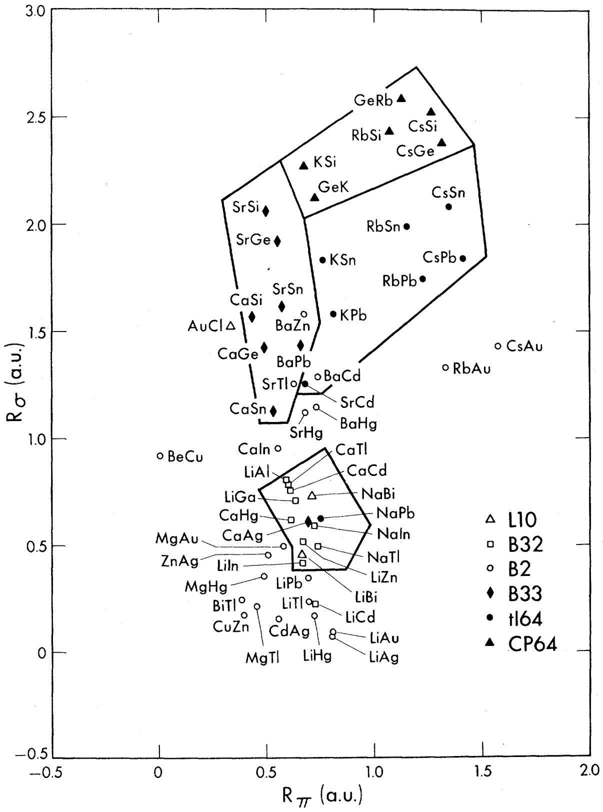

FIG. 2. R_σ vs R_π plot for the suboctet binary compounds. The separation lines are included for convenience.

provide a better structural sensitivity.[12]

The separation of the suboctet compounds works well not only for the two broad classes of bcc-like structures (full symbols) and the anion-valence coordination compounds (open symbols) but also for a large part of the various space groups appearing in these systems. Of the exceptions we note that AuCl (L10), CaAg (B33), and NaPb (tI64) have unusual properties.[13]

In order to study the quality of our first-principles potentials away from the turning-point regions, we apply it to electronic structure problems which are sensitive to lower-momentum components. A nonlocal ($l = 0, 1, 2$) self-consistent band study on Si, using the Kohn-Sham exchange and the free-electron correlation potential, yields results that agree very well with all-electron first-principles calculations and with photoemission studies. We obtain a bandwidth of 12.40 eV (observed 12.4 ± 0.6 eV) while the locations of the high-symmetry valence states are L_{3v} (1.39 eV), X_{4v} (3.13 eV), $L_{1,v}$ (7.09 eV), $L_{2',v}$ (9.85 eV), and $\Sigma_{1,\mathrm{min}}$ (4.80 eV), compared with the observed values[14] of 1.2 ± 0.2, 2.9 ± 0.3, 6.4 ± 0.4, 9.3 ± 0.4, and 4.7 ± 0.3 eV. The "forbidden" [222] x-ray scattering factor is $0.112e$/atom, compared with the observed value of 0.119. The ground-state charge density has the expected anisotropy,[15] i.e., elongated parallel to the band axis, with an anisotropy ratio of 1.62, compared with the observed value[15] of ~1.4–1.5 and the self-consistent empirical pseudopotential value of 0.8 (local) and 1.2 (nonlocal, non-self-consistent[16]). We have performed similar studies on Ge [12] and Mo [17] and obtained comparable results. We conclude from the present study that the density-functional pseudopotential approach correctly describes both the valence electronic properties of atoms, semiconductors, and transition metals, and contains the essential elements for a crystal-phase stability theory. Although these have been obtained in numerical form, their essential features can be cast in the simple analytic form $-Z_v/r + B_l(1-\gamma_l r) + l(l+1)/2r^2$ used by Andreoni *et al.*[8] as can be evidenced from the similarity of the radii for the first-row atoms.[18] This would enable a convenient use of these potentials for a wide range of electronic and structural properties.

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[18]Our r_s values for the first-row atoms of 0.985, 0.64, 0.48 0.39, 0.33, 0.285, 0.25, and 0.22 a.u. are very similar to those of Ref. 8: 1.01, 0.66, 0.49, 0.39, 0.33, 0.28, 0.25, and 0.22 a.u. Similarly, the present r_p values for these atoms of 1.46, 0.44, 0.315, 0.25, 0.21, 0.175, 0.155, and 0.14 are close to the values of Ref. 8: 0.84, 0.41, 0.28, 0.22, 0.18, 0.15, 0.13, and 0.12. The method of Ref. 8 is however limited at present to first-row atoms only.

Thermodynamic Determination of Work Functions of Bound Multiexciton Complexes

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We present direct thermodynamic measurements of the work functions (φ) of bound multiexciton complexes in Al-, B-, and P-doped Si. We find that the value of φ differs in a number of cases from those obtained by assuming ground-state to ground-state transitions for some of the lines seen in luminescence. All the measured values of φ are found to be less than the work function for the electron-hole liquid.

In this Letter we report on a direct thermodynamic measurement of the work functions of bound multiexciton complexes (BMEC)[1,2] in Si:B, Si:Al, and Si:P. For high exciton number, m, the measured values of the work functions, φ_m, are significantly smaller than those previously assigned on the basis of assuming that some of the lines in the luminescence are the result of ground-state to ground-state (G-G) transitions. Our results eliminate the difficulty of explaining the magnitude of the φ_m [greater than $\varphi_{\rm EHL}$ in the electron-hole liquid (EHL)[3]] found in the spectroscopic results.

Previous works on Si:Al and Si:Ga have firmly established that two excitons bind to the acceptor and the position of the G-G transition for the $m=2$ BMEC.[4-7] (Here m labels the number of excitons bound in a complex, i.e., $m=1$ is a BE, etc.) Kirczenow[8] has proposed a shell model (SM) for the BMEC in which some of the lines result from decay into excited states.[9] After some initial successes in explaining the observed line

