PHYSICAL REVIEW B VOLUME 15, NUMBER 10 10 MAY 1977

Ab initio effective potentials for silicon*

Antonio Redondo, William A. Goddard, III,[†] and T. C. McGill
Arthur Amos Noyes Laboratory of Chemical Physics[‡] *and Harry G. Steele Laboratory of Electrical Sciences, California Institute of Technology, Pasadena, California 91125*

(Received 26 April 1976)

We report an effective potential (EP) for replacing the ten core electrons in calculations on the Si atom. This potential was obtained directly from *ab initio* calculations on the states of Si atom and no empirical data or adjustable parameters are used. These *ab initio* effective potentials are tested by carrying out Hartree-Fock, generalized-valence-bond, and extensive configuration-interaction calculations on various molecules. We considered Si, SiH_3, Si_2, and H_3SiO_2 and calculated excitation energies, ionization potentials, and electron affinities both using the EP and without the EP (*ab initio*). In essentially all cases the agreement is to better than 0.1 eV, providing strong evidence that the EP adequately represents the Si core.

I. INTRODUCTION

The idea of using a pseudopotential to replace the core electrons in quantum-mechanical calculations of the electronic wave functions of atoms, molecules, and solids in now well established. The first attempts consisted of the work of Hellmann and Gombâs[1] in the mid-thirties. They realized that these pseudopotentials should incorporate the effects of the Pauli principle in order to avoid the collapse of the valence electrons into the core region. This was put on a sound basis by Phillips and Kleinman[2] in 1959. This work, together with that of Heine and collaborators,[3] initiated a vast series of papers on the applications of pseudopotentials to the electronic structure of solids.[4] These successes also reawakened interest in applying this approach to molecules and atoms.[5]

Although the basic idea in the pseudopotential method is to construct a (simple) operator that reproduces the effect of the core electrons of a given atom on the valence electron, there are a number of approaches to determine the specific form of the pseudopotential. The most common procedure (with many variations) is to select a simple functicnal form for the potential and then to adjust the several parameters in this potential to fit the experimental energy levels of the atom or the band structure of the solid while requiring the pseudopotential to be weak (leading to orbitals with minimal numbers of nodes). The alternate approach is to use only theoretical information in determining the potential, requiring the core potential to reproduce the results of *ab initio* calculations. Our approach is of this latter category (the method of Melius and Goddard[6,7]); we choose the core potential so as to reproduce the *shapes and energies* of *ab initio* valence orbitals. The resulting core potential is referred to as the *ab initio* effective potential or more simply as the EP. Such effective potentials have been previously developed for Li, Na, and K atoms[6] and for Fe and Ni atoms,[8] and applied to a number of molecules containing these atoms. Here we report the effective potential for the core electrons of Si, which we have applied to a number of complexes representing the surface of crystalline silicon. We will assess the accuracy of the effective potential by comparing the results of *ab initio* and effective-potential calculations on the ground and excited states of Si_2, SiH_3, and SiH_3O_2.

The interactions of the valence electrons are handled just as in *ab initio* calculations. Appropriate basis functions are placed on the various centers and the molecular integrals are evaluated. These integrals are then used for self-consistent Hartree-Fock (HF) or generalized-valence-bond (GVB) calculations and ultimately in configuration-interaction (CI) calculations to include various electron-correlation or many-body effects. A special aspect of our approach is that we calculate total energies directly so that we can determine the potential surfaces and geometries for the various excited states.

Since the shapes of the valence orbitals are described correctly, we expect the overlap between orbitals on various centers to behave properly and hence for bond energies and geometries to be well described.

Excitation energies, ionization potentials, and electron affinities are obtained by solving directly for the total energies of each state and taking the difference. Consequently, one can distinguish between the different multiplet eigenstates of the molecule (usually not possible with standard solid-state pseudopotential methods[9]). Another advantage of the present method is that since we include electron-correlation effects explicitly, we can describe processes that involve bond formation or bond breaking.

Section II contains a comparison of the results obtained for Si_2, SiH_3, and SiH_3O_2 using the effective potential with those obtained by full electron *ab initio* calculations. The method used in deriving the effective potential is described in Sec. III, while specific details of the Si effective potential are presented in Sec. IV, along with a further comparison between the *ab initio* and effective-potential calculations. In addition in Sec. IV we include a simplified (but less accurate) version of the effective potential to be used for large complexes.

II. COMPARISON OF THE RESULTS OF EFFECTIVE-POTENTIAL AND *AB INITIO* CALCULATIONS

Before embarking on a description of the calculational details for the Si effective potential, we will summarize some of the results of the comparisons between the EP and *ab initio*[10] calculations on molecules. This will put into perspective the procedure and what we want to obtain from it. We start with self-consistent *ab initio* Hartree-Fock calculations of the electronic wave functions of the Si atom (both the ground and an excited state). From this *ab initio* calculation (using the method described in Sec. III) we obtain an effective potential without the introduction of any experimentally determined parameters. It is this potential that we have used in the calculations below.

As summarized in Table I we carried out both 28-electron *ab initio* calculations and eight-electron EP calculations for the electronic states of the Si_2 molecule (at the experimental equilibrium geometry[11] for the ground state). The low-lying states considered here have either two or four electrons in the π orbitals and are denoted as π^2 and π^4, respectively. The second and third columns show the excitation energies obtained from self-consistent GVB[12] calculations performed on the ground state ($^3\Sigma_g^-$) and the lowest-lying excited state ($^1\Sigma_g^+$). The fourth and fifth columns compare the excitation energies obtained from CI calculations on the low-lying excited states of Si_2. In these CI calculations we included all appropriate excitations within the space spanned by the GVB orbitals for the $^3\Sigma_g^-(\pi^2)$ or $^1\Sigma_g^+(\pi^4)$ states, leading to ~200 spin eigenfunctions of the proper spatial symmetry for each CI calculation. In all cases the *ab initio* and effective-potential calculations lead to excitation energies agreeing within 0.1 eV for the CI wave functions. It is important to note that even for those states that are close in energy, the ordering is not changed in the effective-potential calculations. Since there are numerous states of

TABLE I. Excitation energies for various states of Si_2 ($R=4.244a_0$). All energies in eV.

State	GVB[a] *Ab initio*	GVB[a] Effective potential	CI[b] *Ab initio*	CI[b] Effective potential	Number of configurations[g]
$^3\Sigma_g^-(\pi^2)$	0.0[c]	0.0[d]	0.0[e]	0.0[f]	248
$^1\Sigma_g^+(\pi^4)$	0.285	0.218	0.140	0.070	167
$^1\Delta_g(\pi^2)$	...	...	0.513	0.519	217
$^3\Sigma_u^+(\pi^4)$	...	...	1.518	1.409	261
$^1\Sigma_u^-(\pi^2)$	...	...	2.669	2.640	180
$^3\Delta_u(\pi^4)$	...	...	2.930	2.867	261
$^1\Delta_u(\pi^4)$	...	...	4.040	3.962	180
$^3\Delta_g(\pi^4)$	...	...	5.180	5.066	248

[a] The basis sets used were the Si (6*s*4*p*) and the Si (4*s*4*p*) of Table IV. See the Appendix for a brief summary of the GVB wave functions. The $^3\Sigma_g^-$ calculation is GVB(1); that of the $^1\Sigma_g^+$ state is GVB(3).

[b] The CI calculations were based on the SCF valence orbitals from GVB(1) and GVB(3) calculations for the $^3\Sigma_g^-$ state (two electrons in π orbitals or π^2) and the $^1\Sigma_g^+$ state (four electrons in π orbitals or π^4). All triple excitations were included.

[c] Total energy calculated is −577.688 63 hartree.

[d] Total energy calculated is −7.360 94 hartree.

[e] Total energy calculated is −577.740 61 hartree.

[f] Total energy calculated is −7.413 76 hartree.

[g] This is the number of spin eigenfunctions of proper spatial symmetry.

TABLE II. Energies for SiH_3 and SiH_3^+. The geometry is the same as in silane but without one hydrogen atom; $R_{Si\text{-}H}=2.796a_0$, the HSiH bond angle is 109°28′. The basis sets used are the Si $(6s4p)$ and the Si $(2s2p)$ of Table IV, and a $(2s)$ contraction of the three Gaussian hydrogen bases of S. Huzinaga, J. Chem. Phys. 42, 1293 (1965). All energies in eV.

	Ionization potential		Mulliken population per atom			
			Ab initio		Effective potential	
State[b]	*Ab initio*	Effective potential	Si[c]	H	Si	H
SiH_3 $^2A_1$	0.0[a]	0.0[b]	3.50	1.17	3.74	1.09
SiH_3^+ $^1A_1$	8.637	8.470	2.92	1.03	3.04	0.99
Koopmans theorem	9.396	9.124				

[a] Total energy calculated is −290.563 90 hartree.

[b] Total energy calculated is −5.389 86 hartree.

[c] The ten core electrons have been subtracted from the *ab initio* Si population.

various multiplicities and orbital coupling all within a small range of energy, we consider Si_2 to be a stringent test of the adequency of our EP.

Next we consider the SiH_3 molecule (using the experimental geometry of silane[13] but with one hydrogen atom omitted). Here we performed Hartree-Fock self-consistent-field (SCF) calculations on both the ground state of the neutral ($^2A_1$) and the ground state of the positive ion ($^1A_1$), leading to the ionization potentials of Table II. The EP calculation leads to an ionization potential within 0.17 eV of the *ab initio* value. In order to provide an idea of how similar the wave functions are, we compare the Mulliken populations[14] in Table II. Also listed in Table II are the ionization potentials from application of Koopmans theorem. This leads to IP's too high by 0.7 eV for both *ab initio* and EP calculations.

As a final test, we considered the molecule $H_3Si{-}O{-}\dot{O}$, corresponding to the above SiH_3 unit bound to an oxygen molecule (the new bond lengths are 1.64 Å,[15] for SiO and 1.366 Å,[15] for OO while the SiOO bond angle is[15] 125°53′). In these calculations only the Si core is replaced by an EP. Self-consistent GVB calculations (*ab initio* and EP) were carried out on the ground state ($^2A''$), and the CI calculations were carried out within the orbital spaces spanned by these GVB orbitals. The range of the excitation energies, as shown in Table III, is from 0 to 19.6 eV, and in all cases the *ab initio* and effective-potential calculations lead to the same ordering of states as in the *ab initio* calculations.

These results indicate that the excitation energies and ionization potentials obtained with the effective potentials are in excellent agreement with those of the *ab initio* calculations. Since the systems compared here are reasonably distinct, we consider these results to demonstrate the usefulness of our effective potentials.

TABLE III. Energies for various states SiH_3O_2 and $SiH_3O_2^+$. The geometry is as follows: The SiH_3 geometry is the same as in Table II; the O_2 bonded as a peroxy radical to Si atom, eclipsed with one of the hydrogen atoms; $R_{Si\text{-}O}=3.099a_0$; $R_{O\text{-}O}=2.581a_0$; the O-O-Si bond angle is 125°53′. All energies in eV.

	Excitation energy		
State	*Ab initio* CI[a]	Effective potential CI	Number of configurations[b]
		SiH_3O_2	
$^2A''$	0.0[c]	0.0[d]	98
$^2A'$	0.692	0.662	283
$^2A'$	6.600	6.617	283
$^2A''$	7.924	7.850	98
$^2A'$	8.142	8.116	283
$^2A''$	15.419	15.453	98
$^2A'$	16.174	16.172	283
		$SiH_3O_2^+$	
$^3A''$	11.117	11.173	496
$^1A''$	12.210	12.263	316
$^1A'$	12.582	12.613	340
$^1A'$	13.985	14.031	340
$^1A''$	15.447	15.459	316
$^3A'$	15.468	15.493	530
$^3A''$	15.495	15.520	496
$^3A'$	15.771	15.790	530
$^3A''$	17.366	17.415	496
$^1A''$	18.988	19.048	316
$^1A'$	19.556	19.620	340
$^3A'$	19.619	19.638	530

[a] The CI was carried out using the SCF orbitals from GVB(2)-SCF calculations of the $^2A''$ ground state. All double excitations from ground-state configuration into the π orbitals of the O_2 part were included. These calculations were meant as a test of the effective potential as compared with the *ab initio* results and need not represent the most appropriate way of describing the excitations within this molecule.

[b] This is the number of spin eigenfunctions of proper spatial symmetry.

[c] Total energy calculated is −440.297 63 hartree.

[d] Total energy calculated is −155.154 56 hartree.

III. *AB INITIO* EFFECTIVE POTENTIAL

The general form we use for the EP[16] is

$$V^{\mathrm{EP}}(r)=\sum_{l=0}^{\infty} V_l(r)|l\rangle\langle l| \,, \tag{1}$$

centered on each atom whose core is being replaced. Here $V_l(r)$ is a function of the radius only and

$$|l\rangle\langle l| \equiv \sum_{m=-l}^{l} |lm\rangle\langle lm| \tag{2}$$

is a projection operator onto states of angular momentum l with respect to the center of interest. As described below, the $V_l(r)$ are obtained from *ab initio* calculations on various states of the atom; no readjustments are made to fit the molecular systems. Rather, we have in mind that the potential (1) describes the interaction of the atomic core of interest with orbitals on all centers of the system. With this effective potential we then completely eliminate the core orbitals from the system. Consequently, no basis functions for describing the core orbitals are required, considerably simplifying *ab initio* calculations. We do not require that other orbitals be orthogonal to the core being replaced and hence V_l contains components representing the effects of the Pauli principle. As a result, for Si the V_l for $l=0$ and $l=1$ are highly repulsive in the core region, as can be seen from Fig. 1.

The $V_l(r)$ in (1) are fitted to an analytic expansion of the form

$$V_l(r)=\sum_k C_k r^{n_k} \exp(-\zeta_k r^2) \,, \tag{3}$$

for ease in evaluating the multicenter integrals required in molecular calculations. Use of two to five such terms allows an excellent fit to the *ab initio* atomic wave functions.

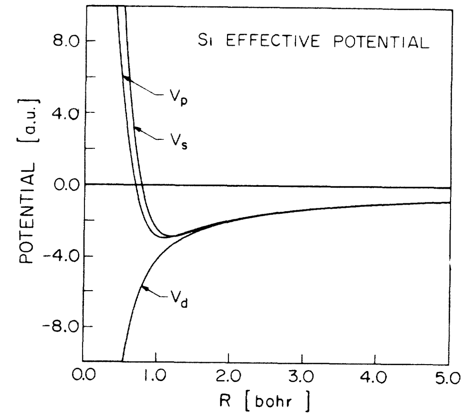

FIG. 1. Si effective-potential components $V_l(r)$. Curves plotted include the nuclear attraction term.

In calculations of the wave functions of molecules (or solids), we must evaluate matrix elements of the form

$$\langle \chi_{\mu A}|V_l(r_B)|\chi_{\nu C}\rangle \,,$$

where the $\chi_{\mu A}$ and $\chi_{\nu C}$ are (Gaussian) basis functions centered on the various nuclei (A,B,C) of the molecule. For terms of the form (3) Melius, Kahn, and Goddard[6,7] have developed formulas, algorithms, and computer programs allowing rapid evaluation of the various one-, two-, and three-centered integrals.

The EP is obtained as follows. We consider the Hartree-Fock equation for the valence orbital of angular momentum l, ϕ_{nl}^{HF},

$$(h+\hat{V}_{\mathrm{core}}^{\mathrm{HF}}+\hat{V}_{\mathrm{val}}^{\mathrm{HF}})\phi_{nl}^{\mathrm{HF}}=\epsilon_{nl}\,\phi_{nl}^{\mathrm{HF}} \,, \tag{4}$$

where $\hat{V}_{\mathrm{core}}^{\mathrm{HF}}$ is the operator (involving Coulomb and exchange operators) describing the interaction of ϕ_{nl}^{HF} with the core.

The first step consists in replacing the Hartree-Fock orbital ϕ_{nl} by the "coreless Hartree-Fock (CHF)" orbital[6] ϕ_{nl}^{CHF} whose amplitude goes smoothly to zero as $r \to 0$. The reasons for doing this are to avoid singularities in the resulting local potential $V_l(r)$ and to minimize the number of basis functions required to describe the valence orbitals. The CHF orbital is obtained by simply mixing Hartree-Fock core orbitals of the same l with ϕ_{nl}^{HF},

$$\phi_{nl}^{\mathrm{CHF}}=\phi_{nl}^{\mathrm{HF}}-\sum_{c=1}^{n-1} C_c\,\phi_{cl}^{\mathrm{HF}} \,, \tag{5}$$

so that $\phi_{nl}^{\mathrm{CHF}}(0)=0$ and the orbital is smooth.[6] (This is analogous to the procedure used in the orthogonalized-plane-wave formalism, where the CHF orbital is replaced by a plane wave.) Once the orbital ϕ_{nl}^{CHF} is determined, one obtains a corresponding Hartree-Fock equation. In it the core and valence operators $\hat{V}_{\mathrm{core}}^{\mathrm{HF}}$ and $\hat{V}_{\mathrm{val}}^{\mathrm{HF}}$ are replaced by new operators $\hat{V}_{\mathrm{core}}^{\mathrm{CHF}}$ and $\hat{V}_{\mathrm{val}}^{\mathrm{CHF}}$, which reflect the fact that $\phi_{\mathrm{val}}^{\mathrm{CHF}}$ may now overlap the core orbitals. That is, Eq. (4) becomes

$$(h+\hat{V}_{\mathrm{core}}^{\mathrm{CHF}}+\hat{V}_{\mathrm{val}}^{\mathrm{CHF}})\phi_{nl}^{\mathrm{CHF}}=\epsilon_{nl}\,\phi_{nl}^{\mathrm{CHF}}. \tag{4'}$$

Note that the orbital energy is still the same while the operator $\hat{V}_{\mathrm{core}}^{\mathrm{CHF}}$ now contains a repulsive part (arising from the Pauli principle) which serves to prevent the collapse of the valence orbitals into the inner shells.

The CHF orbital in (5) is not normalized. After renormalizing, the amplitude of ϕ_{nl}^{CHF} at large r differs from that of ϕ_{nl}^{HF} by just the normalization factor. This means that overlaps and other interaction quantities between orbitals on different centers will be modified by this same (small) factor. We want the transformation from HF orbitals to coreless orbitals to leave intermolecular interactions invariant, and hence we have modified the CHF orbital as follows, leading to the *coreless valence orbital* (CVO). The basis set for the HF orbital is partitioned into the core set (those basis functions important for the 1*s* and 2*s* core orbitals of Si) and the valence set,

$$\varphi^{\rm HF}_{nl} = \sum_{\mu=1}^{M'} C'_\mu \chi'_{\mu l} + \sum_{\mu=M'+1}^{M} C_\mu \chi_{\mu l} , \tag{6}$$

where primes denote the core set. The CVO is taken to have the form

$$\phi^{\rm CVO}_{nl} = \sum_{\mu=1}^{M'} a_\mu \chi'_{\mu l} + \sum_{\mu=M'+1}^{M} C_\mu \chi_{\mu l} , \tag{7}$$

where the valence coefficients are exactly the same as in (6). The conditions on the a_μ of (7) are that (i) $\varphi^{\rm CVO}_{nl}$ as written in (7) must be normalized and (ii) the CVO goes smoothly to zero as r goes to zero. To determine the $\{a_\mu\}$, we set

$$\lim_{r\to 0} \frac{\phi^{\rm CVO}_{nl}(r)}{r^l} = 0 ,$$

and adjust the other $M' - 1$ degrees of freedom so as to minimize the kinetic energy of the orbital. The net result is

$$(h + \hat V^{\rm CVO}_{\rm core} + \hat V^{\rm CVO}_{\rm val})\phi^{\rm CVO}_{nl} = \epsilon_{nl}\varphi^{\rm CVO}_{nl} . \tag{4''}$$

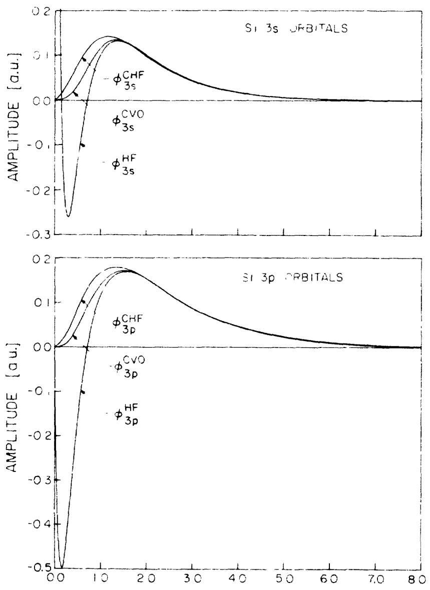

FIG. 2. HF, CHF, and CVO orbitals for the Si atom. (a) 3*s* type; (b) 3*p* type.

In Fig. 2 we compare the HF, CHF, and CVO orbitals for the Si atom. The next step is to replace the operator $\hat V^{\rm CVO}_{\rm core}$ in (4″) with an effective potential $V^{\rm EP}_l(r)$ (that is, a mere function of r), such that the eigenfunction and eigenvalue of (4″) are also the eigenfunction and eigenvalue of (8),

$$[h + V^{\rm EP}_l(r) + \hat V^{\rm CVO}_{\rm val}]\varphi^{\rm CVO}_{nl} = \epsilon_{nl}\,\phi^{\rm CVO}_{nl} . \tag{8}$$

The components of the potential $V_l(r)$ are obtained by projecting (8) onto the basis

$$\langle \chi_\mu | [h + V_l(r) + \hat V_{\rm val} - \epsilon_{nl}] | \varphi^{\rm CVO}_{nl} \rangle \tag{9}$$

and adjusting the parameters in (3) to minimize the deviation of (9) from zero. [More precisely we require that the square of (9) summed over all basis functions is minimized.] In (9) one uses the normal basis functions for an atom plus additional basis functions representing important regions of function space for which $V_l(r)$ is significant. In particular, it is important to add diffuse basis functions to the basis in order to ensure that fitting (9) will lead to the correct long-range behavior of $V_l(r)$. The basis used to solve (9) is included in Table IV [we solve the HF equations for the new basis so that all basis functions are included in the $\phi^{\rm CVO}_{nl}$ of (9)]. After obtaining the effective potential, all basis functions required only for the core can be eliminated (along with the functions added only for fitting the EP).

For those angular momenta l represented in the core, $V_l(r)$ contains a large repulsive component representing the effect of the Pauli principle (the orthogonality of the *ab initio* valence orbital with respect to the core orbitals). For l not represented in the core, $V_l(r)$ is nearly independent of l. Thus for Si we set

$$V_l(r) = V_d(r) \quad \text{for } l \geq 2$$

and rewrite (1) as

$$V^{\rm EP}(r) = V_s(r)|s\rangle\langle s| + V_p(r)|p\rangle\langle p| + V_d(r)\sum_{l=2}^{\infty}|l\rangle\langle l|$$

or

$$V^{\rm EP} = V_d(r) + V_{s-d}|s\rangle\langle s| + V_{p-d}|p\rangle\langle p| , \tag{10}$$

where

$$V_{s-d}(r) = V_s(r) - V_d(r),$$

$$V_{p-d}(r) = V_p(r) - V_d(r),$$

and where s, p, and d indicate $l = 0$, 1, and 2.

IV. EFFECTIVE POTENTIAL FOR SILICON

In Table IV we list the usual basis for *ab initio* calculations on Si and the additional functions used for (9) for determining the potential.

To determine the d potential V_d, we considered the

TABLE IV. Basis sets used in the *ab initio* and effective-potential calculations on the silicon atom. The form of a given basis function χ_μ of angular momentum l is $\chi_\mu = N_\mu \sum_n \alpha_{\mu n} x^p y^q z^s \exp(-\zeta_{\mu n} r^2)$. N_μ is the normalization coefficient; $p=q=s=0$ for an s-type function ($l=0$), $p=1$, $q=s=0$ for a p_x-type function ($l=1$), etc.

		Set used to obtain the EP, Eq. (9) [a]		*Ab initio* double zeta ($6s4p$) basis set [b]		EP ($4s4p$) basis set [c]		EP double zeta ($2s2p$) basis set [d]	
l	$\zeta_{\mu n}$	μ	$\alpha_{\mu n}$	μ	$\alpha_{\mu n}$	μ	$\alpha_{\mu n}$	μ	$\alpha_{\mu n}$
s	26740.0	1	1.0	1	0.002 583				
s	4076.0	2	1.0	1	0.019 237				
s	953.3	3	1.0	1	0.093 843				
s	274.6	4	1.0	1	0.341 235				
s	90.68	5	1.0	1	0.641 675				
s	90.68		...	2	0.121 439				
s	33.53	6	1.0	2	0.653 143				
s	13.46	7	1.0	2	0.277 624				
s	4.051	8	1.0	3	1.0	1	1.0	1	0.043 662
s	1.484	9	1.0	4	1.0	2	1.0	1	−0.274 872
s	0.2704	10	1.0	5	1.0	3	1.0	1	0.653 119
s	0.2704		...		...		...	2	−0.200 408
s	0.099 32	11	1.0	6	1.0	4	1.0	2	0.424 753
s	0.037 31	12	1.0		...		...		...
s	0.014 01	13	1.0		...		...		...
p_x	163.7	14	1.0	7	0.011 498		...		...
p_x	38.85	15	1.0	7	0.077 726		...		...
p_x	12.02	16	1.0	7	0.263 595		...		...
p_x	4.185	17	1.0	7	0.758 262	5	1.0	3	−0.004 717
p_x	4.185		...	8	−1.173 045		...		...
p_x	1.483	18	1.0	8	1.438 335	6	1.0	3	−0.036 542
p_x	0.3350	19	1.0	9	1.0	7	1.0	3	0.345 438
p_x	0.3350		...				...	4	−0.030 736
p_x	0.096 99	20	1.0	10	1.0	8	1.0	4	0.144 725
p_x	0.027 66	21	1.0						
p_x	0.007 890	22	1.0						
d_{xy}	2.973	23	1.0						
d_{xy}	0.7966	24	1.0						
d_{xy}	0.2863	25	1.0						
d_{xy}	0.1154	26	1.0						
d_{xy}	0.049 98	27	1.0						
d_{xy}	0.017 89	28	1.0						
d_{xy}	0.007 211	29	1.0						

[a] This basis set is essentially the ($11s7p$) set of S. Huzinaga [Report from the Department of Chemistry, The University of Alberta (unpublished)] with diffuse and d functions added.

[b] Dunning's double zeta contraction [T. H. Dunning, Jr. (private communication)] used in all *ab initio* calculations.

[c] This set was used in the EP calculations on the Si atom and the Si_2 molecule.

[d] This set is equivalent to an *ab initio* double zeta set. It was used in the EP calculations on SiH_3 and SiH_3O_2.

$$(1s)^2(2s)^2(2p)^6(3s)^1(3p)^2(3d)^1$$

quintet state of Si, solving (4) for the ϕ_{3d} orbital. The V_{s-d} and V_{p-d} potentials were obtained from the ϕ_{3s} and ϕ_{3p} orbitals of the triplet ground state of Si,

$$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2 .$$

In doing this we write

$$V_s = V_d + V_{s-d} ,$$

$$V_p = V_d + V_{p-d}$$

and solve (9) for V_{s-d} and for V_{p-d}.

The resulting potentials are listed in Table V and are plotted in Fig. 1. With just three terms each, we were able to obtain deviations (sums of the squares) of 1.886×10^{-10}, 3.05×10^{-8}, and 8.469×10^{-8} in the least-squares fit to (9) for the V_d,

TABLE V. Parameters for the Si-atom effective potentials. See Eq. (3) for the definitions of n, ζ, and C, and Eq. (10) for the form of the total potential. Quantities are in hartree atomic units. The effective potential for the core electrons also includes a long-range term of $+10/r$. There is also a $-14/r$ term in the h of (4), corresponding to the nuclear attraction. We have deleted the $+10/r$ term from the table with the understanding that the nuclear attraction term in h will be $-4/r$.

	n	ζ	C
V_d	0	0.099 173 6	−0.011 896 20
	−1	0.290 009 0	−0.078 891 66
	−1	3.210 516 9	−3.591 001 10
V_{s-d}	0	3.564 100 9	30.317 562 00
	−2	0.157 085 4	0.248 917 89
	−2	1.847 828 5	4.080 043 40
V_{p-d}	0	4.062 023 7	36.585 571 00
	−2	0.238 986 4	0.453 266 22
	−2	0.968 644 3	0.869 548 14

V_{s-d}, and V_{p-d} potentials, respectively (for the large basis set of Table IV).

Using the EP, the basis on the Si can be modified to eliminate the functions required for describing the core orbitals. This reduces the double zeta valence basis from 18 to eight functions as indicated in Table IV.

We compare in Table VI the results of EP and *ab initio* calculations on various states of Si, Si^-, and Si^+. Here we find errors of the order of 0.01–0.06 eV, quite satisfactory for our purposes. Bear in mind that the EP was determined from fitting the d orbital to a quintet state and the s and p orbitals to a triplet state. No further adjustments were made and hence the good agreement here is already evidence that the potential adequately represents the core electrons. At the HF and GVB level, the lack of complete electron correlations leads to errors in the excitation energies. Thus the experimental triplet-singlet excitation energy is 0.781 eV,[17] and hence 0.275 eV below the GVB value. The experimental ionization potential of Si is 8.149 eV,[17] or 0.864 eV higher than the GVB value, and the experimental electron affinity is 1.385 eV,[18] or 0.769 eV lower than our value.

For comparison in Fig. 3 we show the $3s$ and $3p_x$ orbitals of the ground state (s^2p^2) of Si for the *ab initio* and EP calculations. In Table VII we compare the orbital energies for the EP and the *ab initio* calculations referred to in Table VI. In most cases the difference between the *ab initio* and EP orbital energies was about 0.001 hartree $\simeq$ 0.037 eV. This difference is as high as 0.005 hartree only for some of the GVB correlated pairs. In Tables VIII, IX, and X we show the orbital energies for the Si_2, SiH_3, and SiH_3O_2 SCF calculations, respectively. Here we note that the differences between the *ab initio* and EP are larger than they were in the atomic case. This is to be expected since the effective potential was constructed from the atomic SCF calculations. In the molecular-orbital energies most of the differences between the *ab initio* and EP values are below 0.020 hartree $\simeq$ 0.3 eV, except for some of the GVB correlated pairs in which it is as high as 0.030 hartree. We note, however, that the correlation energies for most of those same GVB pairs (given in Tables VIII–X) agree to better than 0.005 har-

TABLE VI. Energies for various states of Si, Si^+, and Si^- (energies in eV).

		Excitation energy		
Electronic state	Type of wave function[a]	Ab initio SCF	Effective potential	Simplified effective potential
Si^- quartet (s^2p^3)	HF	−0.616	−0.623	−0.030
Si triplet (s^2p^2)	GVB(1)	0.0[c]	0.0[d]	0.0[e]
Si^- doublet (s^2p^3)[b]	GVB(1)	0.684	0.696	1.532
Si singlet (s^2p^2)	GVB(1)	1.056	1.078	1.107
Si quintet (sp^3)	HF	2.893	2.836	2.476
Si^+ doublet (s^2p^1)	GVB(1/3)	7.285	7.276	7.192

[a] The basis sets used were the Si ($6s4p$) and the Si ($4s4p$) sets of Table IV. Both of them were complemented with one diffuse function for each angular momentum type ($\zeta_{\mu n}=0.037\,31$ for s and $\zeta_{\mu n}=0.027\,66$ for p type). See Ref. 12 and the Appendix to the present paper for an explanation of the terms used in this column.

[b] For each state we considered the wave function using real orbitals and orbital symmetry restrictions. Thus this state is not an eigenstate of $\hat{L}^2$.

[c] Total energy calculated is −288.843 78 hartree.

[d] Total energy calculated using the effective potential is −3.676 68 hartree.

[e] Total energy calculated using the simplified effective potential is −3.815 14 hartree.

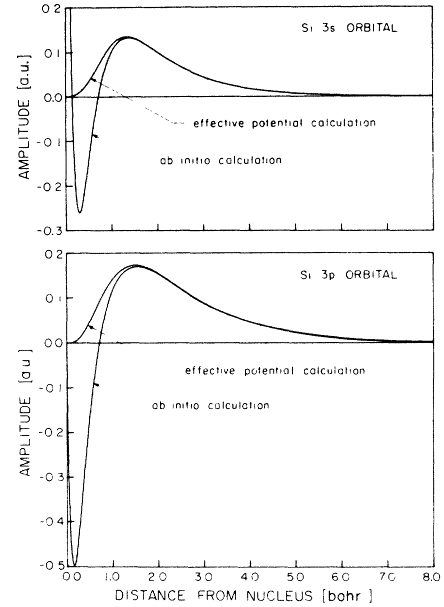

FIG. 3. HF orbitals of Si (^3P) as calculated *ab initio* and using the EP. (a) $3s$; (b) $3p$.

tree ≃ 0.015 eV.

We find that the EP obtained using the above ideas leads to excellent agreement with *ab initio* calculations while eliminating core orbitals and core basis functions. However, although this EP leads to great computational gains, it still requires four basis functions of each type (s, p_x, p_y, p_z) on each Si. For use in our studies of large clusters we have also developed a much cruder, simplified EP (SEP) adjusted so as to require only two basis functions per type per center. In this case we eliminated all core functions from (7), leading to a smooth valence orbital with finite amplitude at the nucleus. The parameters for the SEP are listed in Table XI. Since the orbital is finite at the nucleus, the SEP is much less repulsive at small r than the EP. A plot of this potential is shown in Fig. 4. Table VI compares values of energies obtained with this SEP and *ab initio* calculations for the Si atom.

For band calculations on solids using plane-wave expansions, an overriding consideration is the reduction of the number of plane-wave components. Thus, for such studies the SEP is likely to be more useful than the EP.

V. CONCLUSIONS

These results are very encouraging. The effective potential produces wave functions of *ab initio* quality, as well as very good agreement in the energy quantities of molecular and atomic systems.

TABLE VII. Comparison of orbital energies for *ab initio* (AI) and effective-potential (EP) calculations for various states of Si, Si$^+$, and Si$^-$. All energies in hartree atomic units.

State		Orbital $3s$	$3p_x$	$3p_y$
Si$^-$ quartet (s^2p^3)	AI	−0.3020	−0.0615	−0.0615
	EP	−0.3028	−0.0620	−0.0620
Si triplet (s^2p^2)	AI	−0.5544	−0.2958	−0.8671
		(0.9904)[b]		(−0.1380)
	EP	−0.5551	−0.2956	−0.8725
		(0.9900)		(−0.1409)
Si$^-$ doublet (s^2p^3)[a]	AI	−0.3187	−0.0586	−0.0272
				(0.7071)[c]
	EP	−0.3199	−0.0593	−0.0275
				(0.7071)
Si singlet (s^2p^2)	AI	−0.5617	−0.2597	−0.8747
		(0.9904)		(−0.1382)
	EP	−0.5629	−0.2590	−0.8804
		(0.9900)		(−0.1412)
Si quintet (sp^3)	AI	−0.7247	−0.3487	−0.3487
	EP	−0.7298	−0.3489	−0.3489
Si$^+$ doublet (s^2p^1)	AI	−0.8661	−0.5817	−1.185
		(0.9819)		(−0.1341)[d]
	EP	−0.8664	−0.5801	−1.189
		(0.9811)		(−0.1370)

[a] See footnote b of Table VI.

[b] Numbers in parentheses indicate CI coefficients of GVB correlated pairs. The wave functions of these pairs have the form $C_1\phi_1^2 + C_2\phi_2^2 + C_3\phi_3^2$, where the C_i (CI coefficients) satisfy $\sum_i C_i^2 = 1$. See Ref. 12 and the Appendix to the present paper.

[c] This orbital is correlated with a $3p_z$ orbital having also $C_i = 0.7071$.

[d] This orbital and a $3p_z$ orbital like it correlate the $3s$ orbital in a GVB(1/3) wave function.

It must also be noted that since the wave functions obtained with the effective potential are smooth at the core, we can reduce considerably the number of primitive functions on the basis sets employed. This produces an appreciable reduction of cost in the calculation of the integrals. A further reduction in cost (for large complexes) is obtained when one uses the simplified effective potential for atoms that are not actively involved in the calculation (e.g., "bulk" atoms when calculating surface properties). Besides this, one gets the corresponding reduction in the SCF costs due to the smaller number of electrons involved.

ACKNOWLEDGMENTS

We gratefully acknowledge an IBM Graduate Fellowship (A.R.) and an Alfred P. Sloan Memorial Foundation Research Fellowship (T.C.M.).

TABLE VIII. Comparison of orbital energies for *ab initio* and effective-potential calculations for the $^3\Sigma_g^-$ and the $^1\Sigma_g^+$ states of Si_2 ($R=4.244a_0$). All energies in hartree atomic units.

	$^3\Sigma_g^-$ *Ab initio*	$^3\Sigma_g^-$ Effective potential	$^1\Sigma_g^+$ *Ab initio*		$^1\Sigma_g^+$ Effective potential	
	A. Orbital energies					
ϵ_{σ_g}	−0.6613	−0.6678	−0.6829		−0.6843	
ϵ_{σ_g}	−0.3374 [a]	−0.3303	−0.6648 [a]		−0.6675	
ϵ_{σ_u}	−0.4728	−0.4732	−0.4749 [a]		−0.4761	
$\epsilon_{\pi_{ux}}$	−0.3104	−0.3116	−0.2972 [a]		−0.2976	
	B. GVB pair quantities [b]					
	Bond pair		π bonds (π_x and π_y)	σ nonbonding pair	π bonds (π_x and π_y)	σ nonbonding pair
C_2	−0.1118	−0.1147	−0.2982	−0.9774	−0.2990	−0.9773
S_{ab}	0.7977	0.7931	0.5239	0.6445	0.5228	0.6434
ΔE	0.0094	0.0095	0.0278	0.0424	0.0278	0.0202

[a] This orbital is the first natural orbital of a correlated pair. See Refs. 12 and 19.

[b] The wave function for a correlated pair has the form $C_1\phi_1^2+C_2\phi_2^2$; C_2 is the CI coefficient for the second natural orbital ($C_1^2+C_2^2=1$); ΔE is the correlation energy of the pair; S_{ab} is the overlap of the GVB orbitals of the pair. See Ref. 12 and the Appendix to the present paper.

APPENDIX: GENERALIZED-VALENCE-BOND (GVB) WAVE FUNCTIONS

In order to clarify the discussions of wave functions in this paper we include in this Appendix a brief summary of the GVB wave functions. For further details the reader should consult Refs. 12 and 19.

Consider a two-electron system such as H_2 or the He atom. The Hartree-Fock wave function has the form

$$\Phi^{HF}(1,2)=\mathcal{A}[\phi(1)\phi(2)\alpha(1)\beta(2)]$$
$$=\phi(1)\phi(2)[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\,. \tag{A1}$$

where $\mathcal{A}$ is the antisymmetrizer. The optimum orbitals are obtained by solving the resulting variational equation

$$H^{HF}\phi=\epsilon\phi\ , \tag{A2}$$

where

$$H^{HF}=h+J_\phi\ ,$$

h is the one-electron Hamiltonian, and J_ϕ is the Coulomb potential for an electron in orbital ϕ.

In the GVB wave function for two electrons one allows each electron to have its own orbital; thus

$$\Phi^{GVB}(1,2)=\mathcal{A}\{\phi_a(1)\phi_b(2)[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\}$$
$$=[\phi_a(1)\phi_b(2)+\phi_b(2)\phi_a(1)]$$
$$\times[\alpha(1)\beta(2)-\beta(1)\alpha(2)], \tag{A3}$$

where ϕ_a and ϕ_b are generally nonorthogonal. Applying the variational principle to the GVB wave function leads to the equations

TABLE IX. Orbital energies for SiH_3 and SiH_3^+. All energies in hartree atomic units.

Orbital energies	SiH_3 $^2A_1$ *Ab initio*	SiH_3 $^2A_1$ Effective potential	SiH_3^+ $^1A_1$ *Ab initio*	SiH_3^+ $^1A_1$ Effective potential
$\epsilon_{a'}$ [a]	−0.7137	−0.7110	−0.9981	−0.9965
$\epsilon_{a'}$ [a]	−0.4823	−0.4802	−0.7559	−0.7548
$\epsilon_{a'}$ [b]	−0.3453	−0.3353	···	···
$\epsilon_{a''}$ [a]	−0.4822	−0.4801	−0.7559	−0.7548

[a] Doubly occupied orbital.

[b] Singly occupied orbital.

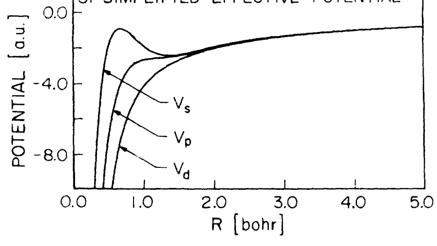

FIG. 4. Si simplified-effective-potential components $V_l(r)$. Curves plotted include the nuclear attraction term.

TABLE X. Orbital energies for the $^2A''$ ground state of SiH_3O_2. The basis sets used are the Si (6s4p) and the Si (2s2p) of Table IV and the H (2s) and O (4s2p) of T. H. Dunning, Jr., J. Chem. Phys. 53, 2823 (1970); and S. Huzinaga, *ibid.* 42, 1293 (1965). All energies in hartree atomic units.

	Ab initio	Effective potential
	A. Orbital energies	
$\epsilon_{a'}$	−20.6740	−20.6777
$\epsilon_{a'}$	−20.6181	−20.6148
$\epsilon_{a'}$	−1.3737	−1.3771
$\epsilon_{a'}$	−1.0588	−1.0638
$\epsilon_{a'}$	−0.7313	−0.7293
$\epsilon_{a'}$	−0.5940	−0.5972
$\epsilon_{a'}$	−0.5099	−0.5084
$\epsilon_{a''}$	−0.6345	−0.6367
$\epsilon_{a''}$	−0.4910	−0.4911
$\epsilon_{a''}$ [a]	−0.6172	−0.6207
	B. For GVB pairs [b]	
	a. Si-O bond	
ϵ_{1NO}	−0.7721	−0.7691
C_2	−0.0852	−0.0881
S_{ab}	0.8424	0.8376
ΔE	−0.0142	−0.0147
	b. O-O bond	
ϵ_{1NO}	−0.7871	−0.7909
C_2	−0.1639	−0.1637
S_{ab}	0.7151	0.7154
ΔE	−0.0397	−0.0396

[a] This orbital is singly occupied.

[b] 1 NO and 2 NO indicate the natural orbitals of the correlated pair, $C_1\phi_{1NO}^2 + C_2\phi_{2NO}^2$; C_2 is the CI coefficient ($C_1^2 + C_2^2 = 1$); ΔE is the correlation energy of the pair; S_{ab} is the overlap of the GVB orbitals of the pair. See Ref. 12 and the Appendix to the present paper.

$$H_a^{\mathrm{GVB}}\phi_a = \epsilon_a\phi_a, \quad H_b^{\mathrm{GVB}}\phi_b = \epsilon_b\phi_b, \tag{A4}$$

which must be solved for the optimum orbitals. In solving for these orbitals it is generally more convenient to transform the spatial part of (A3) to the natural orbital (NO) form

$$N(\phi_a^{(1)}\phi_b^{(2)} + \phi_b^{(1)}\phi_a^{(2)}) = C_1\phi_1(1)\phi_1(2) + C_2\phi_2(1)\phi_2(2), \tag{A5}$$

TABLE XI. Parameters for the Si-atom simplified effective potentials. Quantities are in hartree atomic units. See caption to Table V.

	n	ζ	c
V_d	0	0.099 173 6	−0.011 896 20
	−1	0.290 009 0	−0.078 891 66
	−1	3.210 516 9	−3.591 001 10
V_{s-d}	0	1.901 65	14.714 8
	0	0.253 28	0.195 044
V_{p-d}	0	1.310 07	5.870 41
	0	0.192 52	−0.059 582 2

where

$$\begin{aligned} \phi_1 &= (\phi_a + \phi_b)/D_1, \\ \phi_2 &= (\phi_a - \phi_b)/D_2 \\ C_2/C_1 &= (1-S)/(1+S), \\ S &= \langle\phi_a|\phi_b\rangle, \\ C_1^2 + C_2^2 &= 1, \end{aligned} \tag{A6}$$

and N, D_1 and D_2 are suitable normalization constants. Since ϕ_1 and ϕ_2 are orthogonal, the corresponding variational equations are simpler to solve.

Replacing a HF pair such as in (A1) by a GVB pair such as in (A3) or (A5) accounts for the dominant electron correlation of many-body effects involving these electrons. From the form in (A5) one can say that in the GVB method we solve for the occupied *and* correlating wave function simultaneously and self-consistently.

For a molecular system the correlated orbitals generally localize on or around one or two atoms, leading to what can aptly be interpreted as a bond pair, a core pair, a nonbonding pair, etc. It is possible to selectively correlate only certain pairs; for example, in the *ab initio* wave function for the $^1\Sigma_g^+$ state of Si_2, we might correlate all (four) pairs involving the valence orbitals (3s and 3p) but not correlate the Si core orbitals (1s, 2s, and 2p, ten altogether). Such a wave function would have the form

$$\begin{aligned} &\mathcal{A}[\phi_1^2\phi_2^2\cdots\phi_{10}^2(C_{11}\phi_{11}\phi_{12} + C_{12}\phi_{12}\phi_{11})(C_{13}\phi_{13}\phi_{14} + C_{14}\phi_{14}\phi_{13}) \\ &\quad \times (C_{15}\phi_{15}\phi_{16} + C_{16}\phi_{16}\phi_{15})(C_{17}\phi_{17}\phi_{18} + C_{18}\phi_{18}\phi_{17})\alpha\beta\alpha\beta\cdots\alpha\beta] \end{aligned} \tag{A7}$$

[ten doubly-occupied core orbitals and four GVB correlated pairs (expressed in the (A3) form)]. This wave function would be denoted as GVB(4), indicating that four pairs are correlated.

The programs for calculating the GVB orbitals can also allow additional natural orbitals in an expansion of the form in (A5),

$$C_1\phi_1\phi_1 + C_2\phi_2\phi_2 + C_3\phi_3\phi_3 + C_4\phi_4\phi_4, \tag{A8}$$

and occasionally there are cases where such additional correlations are important; for example, a nonbonding orbital in a negative ion (CH_3^-). Such a wave function for two electrons is denoted as GVB(1/4) indicating 4 NO's for describing one electron pair. For a many-electron wave function the form (A8) would just replace the doubly-occupied orbital of a HF wave function. Physically not more than four to five NO's in an expansion of the form (A8) can be expected to be important, corresponding, for example, to in-out (1) and angular correlations (3) of some doubly occupied orbital.

---

*Supported by a grant, DMR 74-04965, from the National Science Foundation and by a starter grant from the Ford Motor Company Fund of the Ford Energy Research Program.

†Partially supported by a grant, CHE 73-05132, from the National Science Foundation.

‡Contribution No. 5324.

[1] (a) H. Hellmann, J. Chem. Phys. 3, 61 (1935); (b) P. Gombás, Z. Phys. 94, 473 (1935).

[2] J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

[3] (a) M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961); (b) B. J. Austin, V. Heine, and L. J. Sham, *ibid.* 127, 276 (1961).

[4] For a review, see the following (and the references cited therein): (a) W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966); (b) M. L. Cohen and V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 37.

[5] For a review, see (a) J. D. Weeks, A. Hazi, and S. A. Rice, Adv. Chem. Phys. 16, 283 (1969); (b) J. N. Bardsley, Case Studies At. Phys. 4, 299 (1974).

[6] C. F. Melius and W. A. Goddard III, Phys. Rev. A 10, 1528 (1974).

[7] Earlier work on related approaches is summarized in (a) L. R. Kahn and W. A. Goddard III, J. Chem. Phys. 56, 2685 (1972); (b) idem. Chem. Phys. Lett. 2, 667 (1968); (c) L. R. Kahn, Ph.D. thesis (California Institute of Technology, 1971) (unpublished).

[8] C. F. Melius, B. D. Olafson, and W. A. Goddard III, Chem. Phys. Lett. 28, 457 (1974).

[9] See, for example, M. L. Cohen, M. Schlüter, J. R. Chelikowsky, and S. G. Louie, Phys. Rev. B 12, 5375 (1975).

[10] By *ab initio* we mean a calculation in which all the electrons of the system are taken into account and all energy quantities are calculated exactly.

[11] B. Rosen, *Selected Constants—Spectroscopic Data Relative to Diatomic Molecules* (Pergamon, New York, 1970).

[12] (a) W. J. Hunt, P. J. Hay, and W. A. Goddard III, J. Chem. Phys. 57, 738 (1972); (b) W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, Acc. Chem. Res. 6, 368 (1973).

[13] D. R. Boyd, J. Chem. Phys. 23, 922 (1955).

[14] R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955); 23, 1841 (1955).

[15] W. A. Goddard III, A. Redondo, and T. C. McGill, Solid State Commun. 18, 981 (1976).

[16] A similar form for the effective potential was used by V. Heine and I. Abarenkov [Philos. Mag. 9, 451 (1964)]. They used $V_l(r) = -A_l(E)$, $r < R_M$, $V_l(r) = -Z/r$, $r \geqslant R_M$, where $A_l(E)$ is a constant that depends on the orbital energy E of the eigenstates of the ion core of charge Z. R_M is the core radius.

[17] C. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circular 467 (U. S. GPO, Washington, D. C., 1949), Vol. I.

[18] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 439 (1975).

[19] W. J. Hunt, T. H. Dunning, Jr., and W. A. Goddard III, Chem. Phys. Lett. 3, 606 (1969).