

Core effective potentials for Ga, Ge, and As

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We report effective core potentials and the corresponding valence orbitals for Ga, Ge, and As. These potentials were obtained using the shape and Hamiltonian-consistent procedure in which the core portions of the atomic valence orbitals are chosen such that the valence orbital amplitude in the valence region is not changed, while the orbital and valence-valence Coulomb and exchange interactions are maintained at their *ab initio* values.

I. INTRODUCTION

Recently we have developed¹⁻³ *ab initio* effective core potentials for Ga, Ge, and As that have been used successfully for a number of studies,³⁻¹⁰ mainly directed toward models of semiconductor interfaces. This paper reports the details of these potentials.

II. METHOD

For Ga, Ge, and As, the effective core potential replaces the (Ni) core orbitals,

$$[\text{core}] = (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}, \quad (1)$$

reducing the system to three, four, or five valence electrons, respectively. A series of previous studies^{1,11-13} on effective potentials led to the following "shape and Hamiltonian-consistent" (SHC) procedure of Rappé *et al.*¹:

(a) The variational equations for the (all-electron) valence Hartree-Fock (HF) orbitals are written as

$$(h + \hat{V}^{\text{core}} + \hat{V}_l^{\text{val}})\phi_l = \epsilon_l \phi_l, \quad (2)$$

where ϕ_l is the usual $4s$ or $4p$ orbital (h is the one-electron part of the Hamiltonian).

(b) The *ab initio* orbital ϕ_l is replaced by a smooth (non-negative) orbital $\bar{\phi}_l$, called the *pseudo-orbital*, with two important properties: (i) The long-range amplitude of ϕ_l is not to be changed, and only small changes are allowed in ϕ_l for the valence region. (This is the *shape* condition). (ii) The amplitude of the pseudo-orbital in

the core region is determined by requiring that the valence-valence interaction energy for the pseudo-orbital be the same as that for the *ab initio* orbitals. (This is the *Hamiltonian-consistent* condition.)

(c) With the pseudo-orbital $\bar{\phi}_l$ satisfying the above conditions, the effective core potential U_l^{core} is determined such that the pseudo-orbital $\bar{\phi}_l$ is an eigenfunction of

$$[h + U_l^{\text{core}}(r) + \hat{V}_l^{\text{val}}]\bar{\phi}_l = \epsilon_l \bar{\phi}_l, \quad (3)$$

where ϵ_l is the *ab initio* orbital energy. Our calculations utilized a basis set so that condition (c) was replaced by

$$\langle \chi_\mu | U_l^{\text{core}} | \bar{\phi}_l \rangle = -\langle \chi_\mu | h + \hat{V}_l^{\text{val}} - \epsilon_l | \bar{\phi}_l \rangle, \quad (4)$$

where U_l^{core} is expanded as

$$U_l(r) = \sum_k C_k r^{n_k} e^{-\alpha_k r^2}, \quad (5)$$

and the parameters C_k and α_k are determined by nonlinear, least-squares techniques.¹⁴

The specific procedure followed for these atoms involved the following steps (illustrated for Ge):

(α) An *ab initio* HF calculation was carried out for the ground state of the atom

$$[\text{core}](4s)^2(4p)^2 \quad (6)$$

using a double-zeta quality basis.¹⁵

(β) The SHC pseudo-orbitals were taken to have the form

$$\bar{\phi} = C_c \chi_c + C_{v1} \chi_{v1} + C_{v2} \chi_{v2}, \quad (7)$$

where the basis functions χ_{v1} and χ_{v2} and coeffi-

TABLE I. Effective potentials for Ga, Ge, and As. Each partial effective potential is written as in Eq. (5), $U(r) = \sum_k C_k r^{n_k} e^{-\alpha_k r^2}$, and the total effective potential is given as in Eq. (14), $U_{\text{total}}(r) = U_f(r) + \sum_{i=0}^2 [\Delta U_i(r)] \hat{P}_i$.

Potential	Ga			Ge			As		
	c_k	n_k	α_k	c_k	n_k	α_k	c_k	n_k	α_k
ΔU_s	13.119 260	-2	1.884 067	12.623 680	-2	8.575 316	5.862 105	-2	4.082 090
	7.041 914	0	1.858 196	19.775 810	0	1.664 840	18.483 020	0	1.649 383
				-1.116 690	0	0.718 162	-1.674 258	0	0.798 455
ΔU_p	5.105 778 740	-2	0.448 481 655	5.216 928	-2	0.592 261	5.291 331	-2	0.513 171
	-0.949 652 644	0	0.450 855 527	-0.552 8499	0	0.442 749	-1.287 870	0	0.511 539
ΔU_d	0.905 632 10	0	0.445 322	2.042 462	0	0.665 195	3.411 204	0	0.888 271
U_f	-11.358 770	-1	2.715 349	-11.134 330	-1	3.076 115	-10.946 500	-1	3.446 817
	-1.428 557	0	0.964 682	-1.392 421	0	1.141 209	-1.364 321	0	1.322 435

coefficients C_{v1} and C_{v2} describe the valence and long-range behavior of the orbital, and the functions χ_c and coefficient C_c describe the core shape. The basis function χ_c is taken to have the form of a Gaussian function,

$$\chi_c = N Z_{lm} e^{-\alpha_c r^2}, \quad (8)$$

where Z_{lm} is the appropriate (real) spherical harmonic and N is the normalization coefficient. The terms C_{v1} , χ_{v1} , C_{v2} , and χ_{v2} were set equal to the *ab initio* valence double-zeta values (shape condition).

(γ) The nonlinear parameters α_{4s} and α_{4p} , describing the core amplitude of the valence orbitals [see (7) and (8)], were varied to match closely

the pseudo-orbital valence interaction energies to the corresponding *ab initio* energies (Hamiltonian consistent condition). For Ge these valence interaction energies are

$$E_{4s}^{\text{val}} = J_{4s,4s} + 2J_{4s,4p} - K_{4s,4p}, \quad (9a)$$

$$E_{4p}^{\text{val}} = 2J_{4s,4p} - K_{4s,4p} + J_{4p,4p'} - K_{4p,4p'}. \quad (9b)$$

At each step in the optimization, the coefficients C_c were chosen to normalize each pseudo-orbital without disturbing the coefficients for the valence basis function (shape condition).

(δ) To determine the *4d* pseudo-orbital, we first solved for the *4d ab initio* orbital for the ground state of the

TABLE II. Pseudo-valence-orbitals for Ga, Ge, and As. The basis functions $\chi_{4s,1}$ and $\chi_{4p,1}$ consist of two Gaussian functions contracted together, e.g., $\chi_{4s,1} = d_1 N_1 e^{-\alpha_1 r^2} + d_2 N_2 e^{-\alpha_2 r^2}$, where N_i are normalization constants and d_i are contraction coefficients.

Valence orbital	Basis function	Ga		Ge		As	
		d_i	α_i	d_i	α_i	d_i	α_i
4s	$\chi_{4s,1}$	-0.499 512 591	1.094 6861	-0.537 632 739	1.182 146 63	-0.586 236 729	1.289 043 86
		1.220 364 43	0.1947	1.267 0617	0.2462	1.312 3595	0.3003
	$\chi_{4s,2}$	1.0	0.071 58	1.0	0.092 09	1.0	0.1137
4p	$\chi_{4p,1}$	-0.056 889 9164	0.542 800 821	-0.077 787 6845	0.757 976 808	-0.095 430 0762	0.930 044 157
		1.043 846 02	0.2202	1.056 325 78	0.2795	1.068 867 12	0.3441
	$\chi_{4p,2}$	1.0	0.0613	1.0	0.0834	1.0	0.1068
Polarization function	χ_d	1.0	0.25	1.0	0.30	1.0	0.35

$$[\text{core}](4s)^2(4p)(4d) \quad (10)$$

configuration, where all orbitals except ϕ_{4d} were required to be identical to the orbitals obtained in (6). The d basis set of Ref. 14 was extended to describe $4d$ orbitals by optimizing two additional basis functions¹⁶ to minimize the ground-state energy of (10). The $(4d)$ pseudo-orbital (7) is obtained just as in step (γ) except for the use of

$$E_{4d}^{\text{val}} = 2J_{4s,4d} - K_{4s,4d} + J_{4p,4d} - K_{4p,4d} . \quad (11)$$

(ϵ) The $4f$ orbital was obtained from the ground state of the

$$[\text{core}](4s)^2(4p)(4f) \quad (12)$$

configurations, where all orbitals except ϕ_{4f} were required to be the same as in (6). A basis set consisting of ten basis functions was used to describe the $4f$ orbitals for all three atoms.¹⁷ Since there are no f electrons in the core, the *ab initio* f orbital is already non-negative, and no pseudo-orbital is necessary.

(ξ) Starting with the f orbital, the core effective potential $U_f(r)$ was determined using Eq. (5). Then the d , p , and s effective potentials were written as¹¹

$$U_l(r) = \Delta U_l(r) + U_f(r) , \quad (13)$$

and the correction potential ΔU_l solved as in (c). The resulting effective potential to be used for replacing the Ge core in molecular calculations is then

$$U_{\text{Ge}}(r) = U_f(r) + \sum_{l=0}^2 [\Delta U_l(r)] \hat{P}_l , \quad (14)$$

where \hat{P}_l is an operator that projects away any character that does not have angular momentum l with respect to the Ge center.

III. RESULTS

The final effective potentials for Ga, Ge, and As are given in Table I. To use these potentials for molecular calculations, it is the double-zeta basis functions in Table II that are recommended. In addition, we list polarization functions ($4d$) that should be useful for correlated wave functions.

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¹⁶The resulting d Gaussian exponents for Ga were 0.024 and 0.008, for Ge 0.0255 and 0.0085, and for As 0.0270 and 0.0090.

¹⁷The ten f Gaussian exponents were 7.29, 2.43, 0.81, 0.27, 0.09, 0.03, 0.012 81, 0.005 48, 0.002 34, and 0.001.