The shape and Hamiltonian consistent (SHC) effective potentials

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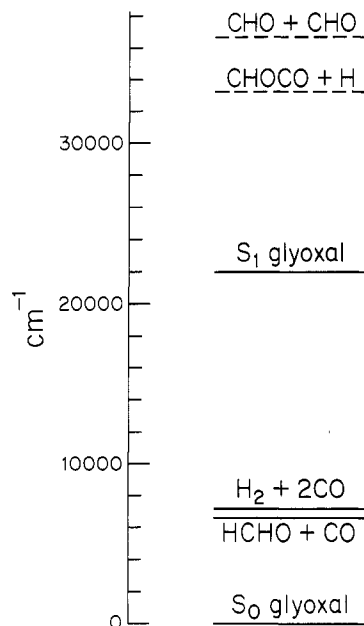**1,324** PUBLICATIONS **67,205** CITATIONS

Figure 7. The ground-state energies of possible dissociation products of glyoxal. The energy of radical products is based on bond energies derived from the known bond lengths in S_0 glyoxal.

S_0^*, the lifetime is placed in the approximate range of 1–10 μs.

Photolysis Products. Evidence but not proof was presented in the Results section that the stable products of the glyoxal decomposition are H_2, CO, and HCHO. If these species are considered to be the dominant photoproducts, then formation of stable products directly from the intermediate would occur by the kinetic steps

$$I \rightarrow HCHO + CO \qquad (j)$$

$$I \rightarrow H_2 + 2CO \qquad (k)$$
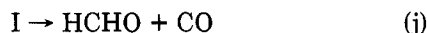
As Figure 7 shows, formaldehyde formed in process j can have up to about 15 000 cm^{-1} of vibrational energy so that the concerted process k might be envisioned as process j

followed by the dissociation of vibrationally hot HCHO.

Several facts show that the dissociation must be more complex than processes j and k. First, the product mix as it appears in Table V is somewhat sensitive to the extent of photolysis. Second and most compelling, no combination of processes j and k can account quantitatively for the product mix in Table V. For example, the approximate doubling of pressure in the 97% photolysis (Table V) cannot be reproduced as long as process k is included, but, on the other hand, indications of substantial H_2 production would require that process.

The second point can be expressed in a more fundamental manner. A mass balance between glyoxal destroyed and products formed cannot be obtained when it is assumed that HCHO (condensable at 77 K) plus H_2 and CO (volatiles) are the only products. A specific search for *cis*-glyoxal by its fluorescence when excited with the 488-nm argon ion line showed that it is not present in significant amounts after nearly complete destruction of *trans*-glyoxal. (The small amount (10^{-5} torr) of *cis*-glyoxal present at thermal equilibrium before photolysis was easily detected.)

If the volatiles are assumed to be CO and H_2, the stoichiometry of the condensable products is by mass balance $C_{1.7}H_{2.0}O_{1.7}$ for the 97% photolysis and $C_{2.3}H_{2.0}O_{2.3}$ for the less secure data of the 25% photolysis. Within the uncertainty of the procedure, the mass balance suggests that the condensables may contain an isomer rather than HCHO. A preliminary study of the condensables by infrared absorption (FT IR) has yet revealed no trace of isomer formation, however, with the only absorptions detected being those of HCHO.[31]

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(31) K. Holtzclaw, private communication, Indiana University.

The Shape and Hamiltonian Consistent (SHC) Effective Potentials

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A new method of replacing core electrons by effective potentials is described. In this approach one assures that (a) the long-range shape of the valence orbital and (b) the average valence–valence part of the SCF Hamiltonians are both unchanged. The resulting shape and Hamiltonian consistent (SHC) potentials are reported for Mg, Al, Si, P, S, and Cl. These potentials lead to more accurate descriptions of molecular wave functions.

Introduction

The idea of using a pseudopotential to replace core electrons in quantum mechanical calculations of the electronic wave functions of atoms, molecules, and solids

is charmingly seductive, not unlike the sirens of Greek mythology. The historical background as well as several theoretically reasonable approaches to this problem are well documented in the literature.[1–10,19a] Despite many

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(1) J. C. Phillips and L. Kleinman, *Phys. Rev.*, **116**, 287 (1959).
(2) W. A. Harrison, "Pseudopotentials in the Theory of Metals", Benjamin, New York, 1966.

successes, there are flaws in the current approaches that lead to errors too large for chemical accuracy. In this paper we present an extension of the previous methods that provides greater accuracy.

Consider, for example, the Si atom. The valence orbitals 3s and 3p are eigenfunctions of the equations

$$H_{3s}\phi_{3s}^{AB} = \epsilon_{3s}\phi_{3s}^{AB} \tag{1}$$

$$H_{3p}\phi_{3p}^{AB} = \epsilon_{3p}\phi_{3p}^{AB} \tag{2}$$

where[11]

$$H_{3s} = h + \hat{V}^{core} + \hat{V}_{3s}^{val} \tag{3}$$

$$H_{3p} = h + \hat{V}^{core} + \hat{V}_{3p}^{val} \tag{4}$$

$$h = \tfrac{1}{2}\nabla^2 - \frac{Z}{r} \tag{5}$$

$$\hat{V}^{core} = \sum_c (2J_c - K_c) \tag{6}$$

$$\hat{V}_{3s}^{val} = J_{3s} + \tfrac{2}{3}(J_{3p_x} + J_{3p_y} + J_{3p_z}) - \tfrac{1}{3}(K_{3p_x} + K_{3p_y} + K_{3p_z}) \tag{7}$$

$$\hat{V}_{3p}^{val} = 2J_{3s} - K_{3s} + \tfrac{1}{2}(J_{3p_x} + J_{3p_y} + J_{3p_z}) - \tfrac{1}{2}(K_{3p_x} + K_{3p_y} + K_{3p_z}) \tag{8}$$

and the sum in (6) is over all five core orbitals 1s, 2s, $2p_x$, $2p_y$, and $2p_z$. These equations, (1) and (2), are incomplete without the orthogonality conditions

$$\langle 3s|1s \rangle = 0$$

$$\langle 3s|2s \rangle = 0 \tag{9}$$

$$\langle 3p_i|2p_i \rangle = 0$$

The basic idea in pseudopotential theory is to combine the orthogonality conditions (9) into the core operator $\hat{V}^{core}$ and to replace this operator by a convenient potential, U^{core}. The general approach for accurate core potentials has been (a) to replace the orthogonal valence orbitals ϕ_{3s} and ϕ_{3p} with smooth, nodeless orbitals ϕ_{3s}^{PS} and ϕ_{3p}^{PS}

$$\phi_{3s}^{PS} = (\phi_{3s} + \lambda_{1s}\phi_{1s} + \lambda_{2s}\phi_{2s})/(1 + \lambda_{1s}{}^2 + \lambda_{1s}{}^2)^{1/2} \tag{10}$$

$$\phi_{3p}^{PS} = (\phi_{3p} + \lambda_{2p}\phi_{2p})/(1 + \lambda_{2p}{}^2)^{1/2}$$

and (b) to find a U^{PS} such that

$$H_{3s}^{PS}\phi_{3s}^{PS} = \epsilon_{3s}\phi_{3s}^{PS} \qquad H_{3p}^{PS}\phi_{3p}^{PS} = \epsilon_{3p}\phi_{3p}^{PS} \tag{11}$$

where the H_i^{PS} are obtained by replacing the $\hat{V}^{core}$ in (3) and (4) with U^{PS}.

In the early applications of Kahn, Goddard, and Melius,[5,6] the procedure for obtaining U^{PS} was simplified by considering the states of the atom having only one valence electron outside the core, allowing an inversion of (11) to obtain

$$U_l^{PS} = \epsilon_{3s} - \frac{h\phi_{3s}^{PS}}{\phi_{3s}^{PS}} \tag{12}$$

Kahn and Goddard[5c] showed that the potential U_l^{PS} depends upon l, suggesting that for molecules the potential be given the form[5,6]

$$U^{PS} = \sum_l U_l(r)\hat{P}_l \tag{13}$$

where $U_l(r)$ is local and $\hat{P}_l$ projects onto angular momentum l. In addition, they found that a range of λ_i in (10) provided reasonable potentials (the condition being that the orbital does not change sign). On this basis, Melius and Goddard[6] developed a procedure using the "coreless Hartree–Fock" (CHF) valence orbital, defined as the smoothest solution of (10) having a node at origin but nowhere else.

In applying this approach to Fe, Olafson discovered that the use of Fe^{7+} orbitals led to core potentials that were not accurate for the neutral system. This led to a modified procedure (Melius et al.[7]) in which the U^{PS} is obtained from (11) for the states of the neutral atom but with the pseudoorbitals used in $\hat{V}_{3s}^{val}$ and $\hat{V}_{3p}^{val}$. This procedure leads to rather accurate potentials and has been used in numerous applications in recent years.[12-19] There are, however, several flaws leading to errors in molecular calculations that we believe can be avoided, as discussed below.

Analysis of Core Potential

Renormalization. Consider the overlap

$$S_{iA,jB} = \langle \phi_{iA}^{AB} | \phi_{jB}^{AB} \rangle$$

of the ab initio valence orbitals on two atoms, A and B.

(3) J. D. Weeks, A. Hazi, and S. A. Rice, *Adv. Chem. Phys.*, **16**, 283 (1969).

(4) J. C. Phillips, "Bonds and Bands in Semiconductors", Academic Press, New York, 1973.

(5) (a) W. A. Goddard, III, *Phys. Rev.*, **176**, 106 (1968); (b) L. R. Kahn and W. A. Goddard, III, *Chem. Phys. Lett.*, **2**, 667 (1968); (c) L. R. Kahn and W. A. Goddard, III, *J. Chem. Phys.*, **56**, 2685 (1972); (d) C. F. Melius, W. A. Goddard, III, and L. R. Kahn, *ibid.*, **56**, 3342 (1972).

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

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

(8) S. Huzinaga, *J. Chem. Phys.*, **51**, 3971 (1969); S. Huzinaga and A. A. Canter, *ibid.*, **55**, 5543 (1971); V. Bonifacic and S. Huzinaga, *ibid.*, **64**, 956 (1976).

(9) U. Wahlgren, *Chem. Phys.*, **29**, 231 (1978); **32**, 215 (1978).

(10) R. N. Dixon, *Theor. Chem.*, **3**, 100 (1978).

(11) J_i and K_i are the usual Coulomb and exchange operators. Thus

$$J_i(r_1) = \int d^3 r_2 \frac{\phi_i{}^*(r_2)\phi_i(r_2)}{r_{12}}$$

$$\hat{K}_i\phi_j(r_1) = \phi_i(r_1)\int d^3 r_2 \frac{\phi_i{}^*(r_2)\phi_j(r_2)}{r_{12}}$$

(12) A. Redondo, W. A. Goddard, III, and T. C. McGill, *Phys. Rev. B*, **15**, 5038 (1977); A. Redondo, Ph.D. Thesis, California Institute of Technology, Dec 1976.

(13) (a) W. A. Goddard, III, A. Redondo, and T. C. McGill, *Solid State Commun.*, **18**, 981 (1976); A. Redondo, W. A. Goddard, III, T. C. McTill, and G. T. Surratt, *ibid.*, **21**, 991 (1977); (b) W. A. Goddard, III, J. J. Barton, A. Redondo, and T. C. McGill, *J. Vac. Sci. Technol.*, **15**, 1274 (1978).

(14) W. A. Goddard, III, and B. D. Olafson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2335 (1975); B. D. Olafson and W. A. Goddard, III, *ibid.*, **74**, 1315 (1977); W. A. goddard, III, and B. D. Olafson in "Biochemical and Clinical Aspects of Oxygen", W. S. Caughey, Ed., Academic Press, New York, 1979, pp 7–123.

(15) R. A. Bair and W. A. Goddard, III, *J. Am. Chem. Soc.*, **99**, 3505 (1977); **100**, 5669 (1978).

(16) T. H. Upton and W. A. Goddard, III, *J. Am. Chem. Soc.*, **100**, 5659 (1978).

(17) S. P. Walch and W. A. Goddard, III, *Surf. Sci.*, **72**, 645 (1978); **75**, 609 (1978).

(18) J. W. Moskowitz, S. Topiol, C. F. Melius, M. D. Newton, and J. Jofri, ERDA Research and Development Report, New York University, Courant Institute of Mathematical Sciences, Department of Chemistry, Jan 1976.

(19) (a) L. R. Kahn, P. Baybutt, and D. G. Truhlar, *J. Chem. Phys.*, **65**, (1976); (b) P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, *ibid.*, **71**, 4495 (1979); (c) P. J. Hay, W. R. Wadt, and L. R. Kahn, *ibid.*, **68**, 3059 (1978).
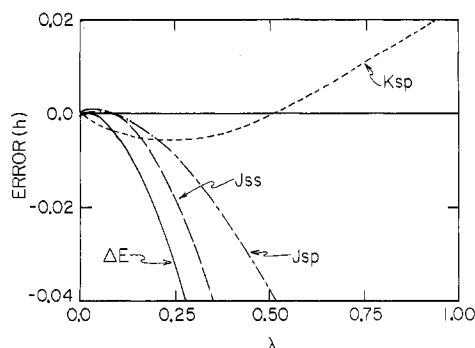
Figure 1. Error in valence transaction energies for various choices of pseudoorbitals.

We would like this overlap to change as little as possible upon using pseudoorbitals

$$\langle \phi_{iA}^{PS} | \phi_{jB}^{PS} \rangle \approx \langle \phi_{iA}^{AB} | \phi_{jB}^{AB} \rangle$$

For reasonable distances, the core of one atom will not overlap the valence electrons on the other atom and hence from (10) we see that

$$\langle \phi_{iA}^{PS} | \phi_{jB}^{PS} \rangle = \langle \phi_{iA}^{AB} | \phi_{jB}^{AB} \rangle / [(1 + \sum \lambda_A{}^2)(1 + \sum \lambda_B{}^2)]^{1/2} \quad (14)$$

where the denominator arises from the renormalization attendant with mixing of core orbitals into the valence orbital. With use of CHF orbitals, this is a small effect (e.g., 0.8% for the 2s orbital of C); however, since bonding effects depend directly upon overlap and related effects, we would prefer to eliminate the renormalization effects.

Modification of the effective potential approach to eliminate renormalization of the pseudoorbital was first suggested by Redondo et al.[12] (1976) and used for a series of calculations on Si-containing systems.[13] The importance of eliminating renormalization and errors in valence–valence interactions in determining effective potentials was employed again by Goddard et al. (1978)[13b] and applied to some third-row (Ga and As) compounds.[13b,25] More recently, Pitzer and co-workers[19b] have developed a similar approach while including relativistic effects.

Valence–Valence Interactions. In the process of smoothing the ab initio orbitals, we necessarily change the density distribution, especially in the core region, and therefore we modify the valence–valence interactions. As a result, the $\hat{V}^{val}$ obtained by using ab initio orbitals is not equal to the $\hat{V}^{val}$ obtained by using pseudoorbitals.

In the various pseudopotential methods, changes are built into the core effective potential so that the orbital energies are correct (for the ground state), but errors may arise in molecular applications if the effective valence state changes (e.g., $3s^2 3p^2 \rightarrow 3s^1 3p^3$). This difficulty has been recognized previously[7,19b,c] though a satisfactory solution was not found.

This is illustrated for C atom in Figure 1. Here we consider a general pseudoorbital

$$\phi_{2s}^{PS} = (\phi_{2s}^{AB} - \lambda \phi_{1s}^{AB})/(1 + \lambda^2)^{1/2} \quad (15)$$

and examine how the various valence–valence integrals, $J_{2s,2s}$, $J_{2s,2p}$, and $K_{2s,2p}$ depend upon λ.

The CHF orbital has $\lambda = 0.22$, and only orbitals with λ greater than or equal to this are nodeless. It is clear that nodeless orbitals lead to large errors. For example, the smoothest pseudoorbital (minimum kinetic energy, $\lambda = 0.267$) leads to errors of $\Delta J_{2s,2s} = 0.564$ eV, $\Delta J_{2s,2p} = 0.285$ eV, and $\Delta K_{2s,2p} = 0.159$ eV.

As is apparent from Figure 1, the best of the nodeless orbitals is the coreless Hartree–Fock orbital that leads to

TABLE I: SHC Basis Sets for Mg–Cl

	α_i	c_i	α_i	c_i
	Mg		Al	
s	0.7641661	−0.3760381	0.9783561	−0.6240356
	0.1110	1.1530197	0.2018	1.2891554
	0.0428	1.0	0.07805	1.0
p	0.1998153	−0.0516078	0.5001926	−0.0962305
	0.1952	1.0515986	0.3040	1.0884666
	0.053	1.0	0.07629	1.0
	Si		P	
s	1.1504763	−0.5589128	1.3539857	−0.5258905
	0.2704	1.3046398	0.3409	2.3081419
	0.09932	1.0	0.1238	1.0
p	0.5978067	−0.052555	0.6895151	−0.0405137
	0.3550	1.0471358	0.4192	1.0374095
	0.09699	1.0	0.1245	1.0
	S		Cl	
s	1.5686128	−0.5206859	1.8283436	−0.5416203
	0.4264	1.3237258	0.5271	1.3484267
	0.1519	1.0	0.1884	1.0
p	0.7658751	−0.0302017	0.8225977	−0.0245481
	0.5218	1.0288117	0.691	1.0240652
	0.1506	1.0	0.1838	1.0

errors of $\Delta J_{2s,2s} = 0.348$ eV, $\Delta J_{2s,2p} = 0.183$ eV, and $\Delta K_{2s,2p} = 0.159$ eV.

The Shape and Hamiltonian Consistent (SHC) Orbitals. In order to improve upon the CHF orbitals as pseudoorbitals, we found it necessary to relax the condition that the pseudoorbital be a linear combination of HF orbitals. The idea here is to require that the pseudoorbital be identical with the original HF valence orbital in the valence region and beyond, but to adjust the shape in the core region so as to satisfy three conditions: (a) keep the orbital nodeless; (b) satisfy the normalization condition; and (c) minimize the error in the valence–valence interaction.

We do this in the following way (illustrated for Si). A good quality Gaussian basis set[20] for Si has 11 s functions and seven p functions of which two of the s functions and two of the p functions describe the valence region and the balance describes the core region. Deleting all but these outer two s or p functions would lead to orbitals that have the correct amplitude in the valence region but that are not normalized. Thus we will construct pseudoorbitals by retaining the (two) valence basis functions with coefficients identical with the HF orbital but with additional core functions chosen so as to satisfy the normalization condition and to describe the valence–valence interactions. In this paper we will restrict ourselves to a single additional core function so that each pseudoorbital (referred to as the SHC orbital) consists of three basis functions

$$\phi_{SHC} = C_c \chi_c + C_{v1} \chi_{v1} + C_{v2} \chi_{v2} \quad (16)$$

where χ_{v1} and χ_{v2} are the (two) valence basis functions, and χ_c is the core function. Since C_{v1} and C_{v2} are from the original HF orbital, there are only two degrees of freedom in the SHC orbital, the coefficient C_c and the orbital exponent (α_c) of χ_c

$$\chi_c = N Y_{lm} r^l e^{-\alpha_c r^2} \quad (17)$$

To determine these two parameters (C_c and α_c) we require (a) that ϕ_{SHC} be normalized and (b) that the average valence–valence interactions

$$\langle \phi_{SHC} | \hat{V}_{val} | \phi_{SHC} \rangle$$

(20) T. H. Dunning, Jr., and P. J. Hay in "Modern Theoretical Chemistry"; H. F. Schaefer, III, Ed., Plenum Press, New York, 1977, Vol. 3, pp 1–27.

TABLE II: Diffuse d Basis Sets for Mg-Cl

Mg	Al	Si	P	S	Cl
8.9782	9.9757	11.0842	12.3157	13.68414	15.2056
3.1745	3.5272	3.9191	4.3546	4.8384	5.376
1.122	1.247	1.3856	1.5396	1.7106	1.9007
0.3968	0.4409	0.4899	0.5443	0.6048	0.672
0.1439	0.1559	0.1732	0.1925	0.2138	0.2376
0.0496	0.0551	0.0612	0.068	0.0756	0.084
0.01754	0.01949	0.0216	0.02406	0.02673	0.0297
0.00620	0.006889	0.0076545	0.008505	0.00945	0.0105
0.002783	0.003092	0.003435	0.003817	0.004241	0.004712
0.000773	0.000859	0.000955	0.001061	0.001179	0.0013124

be the same as for the ab initio orbitals. Condition a ensures that the long-range shape of the orbital be correct, and condition b ensures that the valence Hamiltonian (average valence–valence interactions) is correct. Thus we refer to these orbitals as the *shape and Hamiltonian consistent* (SHC) *orbitals*. For carbon this method leads to errors of $\Delta J_{2s,2s} = 0.041$ eV, $\Delta J_{2s,2p} = 0.041$ eV, and $\Delta K_{2s,2p} = 0.122$ eV, a significant improvement over CHF. Given the SHC orbital, the core potential of which this function is an eigenfunction can be determined just as in previous methods.

Redondo et al.[12] used a related procedure to develop a core potential for Si. They used a form as in (16) with two core orbitals and required that the core functions be chosen to obtain the normalization condition and a zero amplitude at the origin. The remaining degrees of freedom were determined with a smoothness condition. Wadt[21] also used a procedure similar to ref 12 for C and O.

Calculational Details

The overall procedure used to derive the potentials reported herein is as follows:

(a) The initial Hartree–Fock calculation is carried out by using proper spherically summetric fields on the appropriate state using a reasonable basis.[20] This calculation determines the valence shape and energy of the orbitals that the effective potential must reproduce.

(b) Using valence orbitals from (a) evaluate the ab initio two-electron valence–valence interaction energy. For Si this energy is $E_{VS} = J_{SS} + 2J_{SP} - K_{SP}$ for s orbitals, and $E_{VP} = 2J_{SP} - K_{SP} + J_{PP'} - K_{PP}$ for p orbitals.

(c) A single Gaussian s or p function is found to replace all core basis functions such that we obtain the same valence two-electron energy found in (b), while keeping the two-valence basis function coefficients fixed at their ab initio values. These SHC exponents are listed in Table I.

(d) Given the SHC orbitals from (c), we must determine the core effective potentials of which these orbitals are eigenfunctions. Recall that the potential is angular momentum dependent, eq 13. Generally for $l \geq 2$ the potentials are the same (since only $l = 0$ and $l = 1$ are involved in the core), and by using closure[6] (13) can be rewritten as

$$U_{EP} = U_d(r) + (U_s - U_d)\hat{P}_s + (U_p - U_d)\hat{P}_p \quad (18)$$

The U_d potential is the obtained by solving for the lowest excited configuration of the ab initio atom having an occupied d orbital, e.g.

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

for Si but with the restrictions that the 3s, 3p, and core orbitals be the same as in the ground state. We used a

TABLE III: SHC Potentials for Mg-Cl

	$n + 2$	α_i	c_i	α_i	c_i
		Mg		Al	
d	1	3.99353	−5.327025	5.57615	−5.281466
	2	1.50529	−1.979171	2.20257	−2.701409
	1	0.34649	−0.043481	0.58863	−0.094216
p-d	0	0.71279	19.160060	5.76064	29.315620
	2	0.32736	5.392516	0.73949	8.667070
	0	0.20118	−14.426270	0.36425	−5.638679
s-d	0	2.30322	26.419780	3.68515	7.070717
	2	1.05353	29.968060	1.29731	15.207360
	0	0.64389	−20.963640	0.54773	−3.395479
		Si		P	
d	1	7.83060	−5.363329	10.68823	−5.528271
	2	3.06319	−3.721345	4.05005	−4.803538
	1	0.81819	−0.131534	1.08538	−0.169215
p-d	0	2.88429	16.863100	3.15308	11.299300
	2	0.85043	11.113880	0.95719	8.286088
	0	0.45365	−7.922837	0.45970	−4.478919
s-d	0	4.00531	5.595966	4.70869	4.225186
	2	1.52884	17.406740	1.83908	19.081040
	0	0.58277	−2.929172	0.58365	−1.968807
		S		Cl	
d	1	11.81894	−5.424285	12.86483	−5.331313
	2	4.61237	−4.656409	5.12909	−4.407877
	1	1.23883	−0.143630	1.37704	−0.117761
p-d	0	5.42835	13.195500	8.91386	15.154140
	2	1.28475	9.822339	1.49773	9.792946
	0	0.54832	−3.483716	0.57753	−2.237323
s-d	0	7.00722	3.636456	4.56919	3.713000
	2	2.22283	22.709250	2.39514	23.97716
	0	0.58211	−1.437261	0.69924	−1.905195

basis of ten functions to describe these d orbitals. This basis is listed in Table II. Since there are no d orbitals in the core, the U_d potential is obtained directly from ϕ_d.

(e) In solving for the U_s and U_p potentials, we first added additional basis functions selected as follows: If α_1 and α_2 are exponents corresponding to the two valence basis functions ($\alpha_2 < \alpha_1$), we define

$$\zeta = (\alpha_2/\alpha_1)^{1/2}$$

and choose one new function with $\alpha = \zeta\alpha_1$ (the geometric mean between α_1 and α_2) and additional more diffuse functions at $\zeta\alpha_2$, $\zeta^2\alpha_2$, $\zeta^3\alpha_2$, ... A total of nine s and p noncore functions were used in the new basis. Keeping the core orbitals fixed, we set up the s and p valence Hamiltonians for the ground configuration and solved for the valence orbitals using the extended basis.

(f) For the s and p orbitals obtained above, we remove the core basis functions and insert the SHC exponent from step (c). The coefficient of this SHC exponent is determined by holding all nine valence coefficients fixed and then normalizing the orbital.

(g) To determine the U_l effective potential, we require that

$$\langle \chi_\mu | h + \hat{V}_{val,l} - \epsilon_l + U_l | \phi_{val}^{SHC} \rangle = 0 \quad (19)$$

where $\hat{V}_{val,l}$ is the valence Hamiltonian for shell l, ϵ_l is the

(21) W. R. Wadt, Ph.D. Thesis, California Institute of Technology, 1975.

TABLE IV: Comparison of Ab Initio and Effective Potential Calculations on s^2p^n and s^1p^{n+1} states[a]

		AI	SHC	Δ	AI	SHC	Δ
			Mg			Al	
s^2	E_{tot}	−199.5946	−0.7846		−241.8550	−1.8755	
	ϵ_s	−0.2528	−0.2528	0.0000	−0.3895	−0.3896	−0.0001
	ϵ_p				−0.2070	−0.2068	0.0002
s^1	E_{tot}	−199.5255	−0.7146		−241.7667	−1.7873	
	ΔE_{tot}	0.0691	0.0700	−0.0009	0.0883	0.0882	0.0001
	ϵ_s	−0.3384	−0.3378	0.0006	−0.5217	−0.5222	−0.0005
	ϵ_p	−0.1784	−0.1820	−0.0036	−0.2590	−0.2611	−0.0021
			Si			P	
s^2	E_{tot}	−288.8295	−3.6745		−340.6888	−6.3518	
	ϵ_s	−0.5364	−0.5365	−0.0001	−0.6936	−0.6936	0.0000
	ϵ_p	−0.2944	−0.2944	0.0000	−0.3888	−0.3888	0.0000
s^1	E_{tot}	−288.7371	−3.5840		−340.3872	−6.0501	
	ΔE_{tot}	0.0924	0.0905	0.0019	0.3016	0.3017	−0.0001
	ϵ_s	−0.7234	−0.7259	−0.0025	−0.8732	−0.8764	−0.0032
	ϵ_p	−0.3479	−0.3493	−0.0014	−0.3088	−0.3083	0.0005
	$\epsilon_{p'}$				−0.4358	−0.4383	−0.0025
			S			Cl	
s^2	E_{tot}	−397.4683	−9.9453		−459.4377	−14.7258	
	ϵ_s	−0.8755	−0.8754	0.0001	−0.1068	−0.1068	0.0000
	ϵ_p	−0.3915	−0.3906	0.0009	−0.4849	−0.4845	0.0004
	$\epsilon_{p'}$	−0.4752	−0.4761	−0.0009	−0.5627	−0.5642	−0.0015
s^1	E_{tot}	−397.0416	−9.5184		−458.8701	−14.1572	
	ΔE_{tot}	0.4267	0.4269	−0.0002	0.5676	0.5686	−0.0010
	ϵ_s	−0.1023	−0.1026	−0.0003	−0.1169	−0.1171	−0.0002
	ϵ_p	−0.3991	−0.3990	−0.0001	−0.4933	−0.4936	−0.0003
	$\epsilon_{p'}$	−0.5280	−0.5315	−0.0035			

[a] All quantities are in Hartree atomic units (1 hartree 27.2117 eV). A symmetrized Hamiltonian is not used; therefore, singly occupied and doubly occupied p orbitals are different (they are denoted as p' and p, respectively.

ab initio orbital energy, ϕ_l^{SHC} is the orbital being fit [from (e) or (f) above], and χ_μ is the μth basis function. The U_l must satisfy

$$\langle \chi_\mu | U_l | \phi_l^{SHC} \rangle = \langle \chi_\mu | \epsilon_l - h - \hat{V}_{val,l} | \phi_l^{SHC} \rangle$$

We take $U_l(v)$ to have the form

$$U_l(v) = \sum_k c_k r^{n_k} e^{-\alpha_k r^2}$$

and determine the c_k and α_k by a nonlinear least-squares technique (SIMPLEX[22]) to generate the effective potentials. We first determine the U_d potential and then the $(U_s - U_d)$ and $(U_p - U_d)$ potentials. The potentials obtained by the above method are listed in Table III.

Results and Discussion

Table IV shows a comparison of ab initio and effective potential calculations for the s^2p^n and s^1p^{n+1} states of Mg–Cl. The effective potential energy splittings are excellent, differing from the ab initio values by at most 0.05 eV.

The use of these potentials was tested in a number of molecular systems including the following: (a) studies of the geometries and energies of triplet and singlet SiH_2, where comparison with ab initio calculations shows errors

of 0.04 eV in singlet–triplet excitation energies and 0.5° in bond angles;[23] (b) similar studies of CCl_2 where comparison with ab initio calculations shows errors of 0.03 eV in singlet–triplet excitation energies, 0.7° in bond angles, and 0.01 Å in bond distances;[24] (c) models for the (110) surface of GaAs, GaP, AlAs, and AlP.[25] Comparisons with ab initio calculations indicate errors of 0.02 eV in the reconstruction energy and 0.4° in the reconstruction angle.

Our conclusion is that use of the SHC effective potential provides an ab initio quality description of molecular systems.

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