References and Notes

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A Pseudopotential SCF Method for Valence-Only Molecular Calculations

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Abstract: A nonempirical valence-only LCAO–MO–SCF method is presented based on an adaption of the Phillips–Kleinman pseudopotential to replace orthogonality constraints and on representation of the core–valence coulomb and exchange interactions by an exponential screening function. Computation times are greatly reduced compared to full *ab initio* calculations. Results are reported for main-group atoms up to atomic number 36, and for the molecules C_2, Si_2, Ge_2, and PF_3. These are compared to conventional SCF results and, for C_2 and PF_3, with experiment.

Despite rapid advances in computer technology in the last decade, *ab initio* calculations on relatively small molecules containing elements of atomic number greater than 18 (Ar) are still expensive and far from routine. Since the expense of a calculation increases roughly as the fourth power of the number of basis functions, even a 1000-fold increase in computer speed would allow only a six-fold increase in the complexity of a system to be investigated within the same computational time. Thus, investigation of many chemical problems using conventional *ab initio* methods does not seem possible in the near future.

The success of semiempirical MO methods has been largely limited to elements of atomic number less than 10 (Ne), due to lack of reliable spectroscopic data on the heavier elements and to the breakdown of the common approximations for the various integrals. As an example of the latter, most methods take the off-diagonal core-hamiltonian integral H_{ab} as proportional to the overlap integral between orbitals a and b.

$$H_{ab} \sim kS_{ab} \tag{1}$$

Jug[1] has shown that this approximation is poor for p_σ–p_σ integrals over symmetrically orthogonalized orbitals. Equation 1 constrains H_{ab} to have the same sign as S_{ab}, but, according to Jug, this is not necessarily the case at all. This problem is even more severe with integrals over d orbitals. Thus, the prospects for successful simple extension of semiempirical methods to the heavier elements appear dim.

In this paper we will outline a third and potentially much more useful approach for predicting the properties of inorganic compounds. This involves partitioning of the molecule's electronic distribution into "valence" and "core" orbitals. Such a partitioning allows the valence orbitals to be treated by comparatively rigorous *ab initio* techniques, with a minimal amount of labor. The distinction between bonding valence electrons and non-bonding core electrons is widely applied in many fields of chemistry; partitioning techniques use this distinction to its greatest possible computational advantage.

The theory of core–valence separation was widely studied in the early days of quantum chemistry[2-11] and also has been the subject of considerable recent interest.[12-24] In the

Table I. Effect on the Valence-Orbital Energies, ϵ, of a Collapsed-Core Approximation Using Minimal-Slater Basis Sets as Compared to a Full-SCF Calculation (au)

Atom	Full SCF		Core-orthogonal valence		Single-Slater valence	
	ϵ_s	ϵ_p	ϵ_s	ϵ_p	ϵ_s	ϵ_p
C	−0.67749	−0.40162	−0.43701	−0.37650	−1.17507	−0.36602
Si	−0.49231	−0.26977	+0.07224	+0.02941	−0.79525	−0.40373
Ge	−0.45619	−0.23995	+0.39250	+0.15463	−0.66859	−0.33266

following sections we present a semirigorous valence-orbital method, requiring no experimental data as input and with a minimum of adjustable parameters, which should greatly reduce the computation time as compared to a full *ab initio* calculation. Since the core orbitals are not included explicitly, we will refer to this method as NOCOR (neglect of core orbitals).

Method

Assume that a full variational calculation on a particular system leads to a set of orbitals Φ which may be partitioned into a singly-occupied valence orbital ϕ_v and a set of core orbitals Φ_c. These orbitals satisfy the conditions

$$H\phi_c = E_c\phi_c \quad \text{for } \phi_c \in \Phi_c \tag{2}$$

$$H\phi_v = E_v\phi_v \tag{3}$$

$$\langle\phi_c|\phi_v\rangle = 0 \quad \text{for } \phi_c \in \Phi_c \tag{4}$$

As discussed above, it would be useful to be able to treat only the valence orbital. An attempt to perform a variational calculation of ϕ_v alone will fail if the effect of the orthogonality constraint eq 4 is not observed, since ϕ_v would collapse into the core region. Van Vleck[25] called this "the nightmare of the inner shells." Early attempts[26,27] to transform the orthogonality constraints to the operator H were finally put on a sound footing by Phillips and Kleinman[28] in 1959. They showed that eq 2-4 could be transformed to an equivalent equation

$$[H + V^{PK}]\chi_v = E_v\chi_v \tag{5}$$

where χ_v is no longer constrained to be orthogonal to the set Φ_c and is termed the pseudowave function. V^{PK} is the Phillips-Kleinman pseudopotential, a repulsive, nonlocal potential defined as

$$V^{PK}\chi_v \equiv \sum_c |\phi_c\rangle(E_v - E_c)\langle\phi_c|\chi_v\rangle \tag{6}$$

It is easily seen that all ϕ_c are also eigenfunctions of the modified Hamiltonian $[H + V^{PK}]$, but with eigenvalue E_v rather than E_c. Hence the effect of V^{PK} is to make ϕ_v degenerate with all the ϕ_c so that the contributions of the ϕ_c to χ_v are arbitrary within a linear transformation. Any arbitrary χ_v, with no orthogonality constraints, may be employed in a variational calculation without danger of collapse to the core levels. Weeks *et al.*[29] have published an excellent review of the pseudopotential method.

Equation 5 is clearly valid for a Fock operator describing a single valence electron outside of the core, but an extension to a many-valence-electron system within the Hartree-Fock formalism necessitates an approximate treatment. Weeks and Rice[24] and Huzinaga and Cantu[21] have discussed the theoretical problems involved. The difficulty is that valence electron-electron repulsion cannot be treated rigorously due to the failure of the core projection operator $|\phi_c\rangle\langle\phi_c|$ to commute with the operator r_{12}^{-1}. Nonetheless, we have found that useful results for atoms and closed-shell molecules may be obtained if these terms are treated as follows. Let the restricted Hartree-Fock Hamiltonian operator F replace the operator H of eq 2 and 3

$$F\phi_i = \epsilon_i\phi_i \tag{7}$$

$$F \equiv T + U + \sum_v^{\text{valence}} (2J_v - K_v) + \sum_c^{\text{core}} (2J_c - K_c) \tag{8}$$

where T, U, J, and K operators have their usual definitions. For atoms and molecules with open valence shells but closed core shells, a similar expression applies. We assume that any additional perturbation of an open valence shell upon the core will be small. To formulate an equation analogous to eq 6, the following three problems must be considered.

(1) The Phillips-Kleinman pseudopotential (eq 6) requires knowledge of the core orbitals and their eigenvalues. These are precisely those orbitals we wish to avoid calculating. We employ a "frozen-core" approximation, taking the core orbitals and their eigenvalues from atomic SCF calculations. Szasz[30] has examined the frozen-core approximation in relation to pseudopotentials and found that it works quite well. With elements of higher atomic number, the core electrons become increasingly polarizable, however, so that difficulties may arise. We discuss this point in a later section.

(2) The operator F (eq 8) depends explicitly upon the core orbitals. The exact calculation of the core-valence coulomb and exchange integrals is very time consuming; we would prefer to simulate the effect of these integrals in some simpler manner. Other authors[17,19] have used a "collapsed-core" approximation, treating the core orbitals as a point charge coincident with the nucleus. This has also been the general procedure in semiempirical methods. In Table I we present collapsed-core valence eigenvalues for the C, Si, and Ge atoms, using both single-Slater valence orbitals (not orthogonal to the core shells from a full SCF calculation) and the core-orthogonal SCF calculation that includes the core shells. In all these calculations minimal Slater basis sets with atom-optimized exponents[31] were used. No provision for lack of core-valence orthogonality was made in the single-Slater valence-orbital calculations. It is evident that the collapsed-core approximation is uniformly poor and becomes progressively worse with increasing principal quantum number of the valence shell. Fischer-Hjalmars[8] has commented that use of Slater-type valence orbitals not orthogonal to the core orbitals seems to work better than does use of orthogonal SCF orbitals in a collapsed-core approximation. This is due to a cancellation of errors; the neglect of core-valence orthogonality causes the eigenvalues to decrease, while the complete screening of the nuclear charge in the collapsed-core approximation causes them to increase. That such cancellation cannot be relied upon to give chemically significant results is evident from Table I.

Rather than employ a completely collapsed core, we propose an exponential screening function $f(r)$, so that

$$Z_A^{\text{eff}} = Z_A - f(r_A) \tag{9}$$

where

$$\lim_{r_A \to 0} f(r_A) = 0 \tag{10}$$

$$\lim_{r_A \to \infty} f(r_A) = N_c{}^A \tag{11}$$

where $N_c{}^A$ is the number of core electrons on nucleus A. A simple function satisfying these constraints is

$$f(r_A) = (1 - e^{-\alpha_A r_A})N_c{}^A \tag{12}$$

Using a local potential such as this has the considerable advantage of requiring the calculation of only one-electron

Table II. Screening Exponents and Valence Eigenvalues for the Atoms, Calculated in Minimal-Slater Basis Sets

		Full SCF		Core-orthogonal valence			Single-Slater valence		
Atom A	Core electrons	s-Orbital energy	p-Orbital energy	Screening exponent α_A	s-Orbital energy	p-Orbital energy	Screening exponent α_A	s-Orbital energy	p-Orbital energy
Li	2	−0.19489		2.2435	−0.19489		1.9530	−0.19489	
Be	2	−0.30865		3.1194	−0.30865		2.6331	−0.30865	
B	2	−0.48389	−0.30037	4.1777	−0.47822	−0.30604	3.6150	−0.47638	−0.30788
C	2	−0.67749	−0.40162	5.0916	−0.66952	−0.40959	4.4209	−0.66660	−0.41251
N	2	−0.89255	−0.50336	6.0003	−0.88234	−0.51357	5.2224	−0.87837	−0.51754
O	2	−1.15091	−0.50330	6.8963	−1.13883	−0.51538	5.9932	−1.13414	−0.52007
F	2	−1.43064	−0.52641	7.7957	−1.41656	−0.54049	6.7750	−1.41101	−0.54604
Ne	2	−1.73253	−0.56175	8.6972	−1.71638	−0.57790	7.5625	−1.70992	−0.58436
Na	10	−0.17525		2.6204	−0.17525		2.3441	−0.17525	
Mg	10	−0.24097		3.0040	−0.24097		2.6182	−0.24097	
Al	10	−0.34684	−0.17433	3.2693	−0.34679	−0.17439	2.8026	−0.34291	−0.17826
Si	10	−0.49231	−0.26977	3.6719	−0.49292	−0.26916	3.1376	−0.48928	−0.27280
P	10	−0.64336	−0.35847	4.0548	−0.64342	−0.35841	3.4568	−0.63865	−0.36318
S	10	−0.81165	−0.38715	4.4302	−0.81114	−0.38765	3.7216	−0.81065	−0.38815
Cl	10	−0.98855	−0.43917	4.8010	−0.98735	−0.44038	3.9885	−0.99099	−0.43674
Ar	10	−1.17468	−0.50633	5.1775	−1.17240	−0.50868	4.3036	−1.17335	−0.50765
K	18	−0.13951		2.2638	−0.13951		1.6985	−0.13951	
Ca	18	−0.18210		2.5058	−0.18210		1.8643	−0.18210	
Ga	28	−0.33246	−0.16920	3.5980	−0.33420	−0.16740	3.2869	−0.33172	−0.16994
Ge	28	−0.45619	−0.23995	3.8243	−0.45809	−0.23805	3.4693	−0.45495	−0.24120
As	28	−0.59029	−0.31898	4.0448	−0.59214	−0.31713	3.6521	−0.58800	−0.32127
Se	28	−0.71946	−0.32931	4.2580	−0.72125	−0.32751	3.8042	−0.71976	−0.32901
Br	28	−0.86069	−0.36784	4.4698	−0.86233	−0.36615	3.9595	−0.86426	−0.36427
Kr	28	−1.00679	−0.42092	4.6820	−1.00793	−0.41979	4.1363	−1.00962	−0.41811

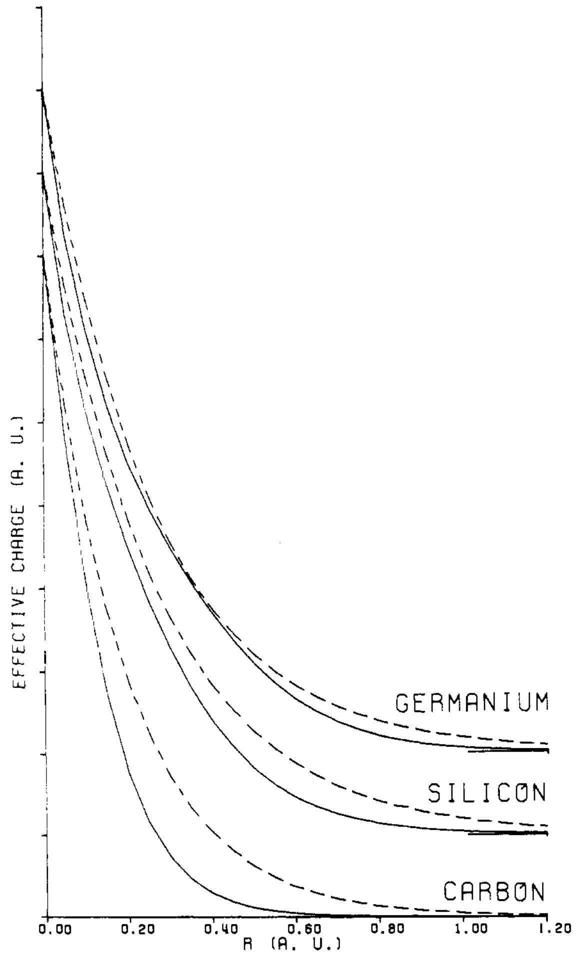

Figure 1. Comparison of the model potentials obtained from fitting the orbital energies (dotted line), with the exact core Coulombic potential, obtained for a minimal Slater basis set (solid line). For comparison purposes, the curves for the carbon, silicon, and germanium atoms are plotted on a normalized linear scale which is set so that each curve ranges from 4 au at infinite distance ($R = \infty$) to Z au at $R = 0$, Z being the atomic number.

integrals. This specific function is chosen because (a) it greatly simplifies evaluating integrals over Slater-type orbitals, (b) it is closely related to the Hellmann potential, whose theoretical justifications are well known,[33] (c) it is found to reproduce atomic orbital energies quite accurately, particularly for heavy elements (*cf.* Table II), and also (d) it satisfies all the conditions suggested by Simons[13] (except angular momentum dependence, which is here incorporated in the V^{PK} term).

In Figure 1, we compare the screening function of eq 12 with the exact coulombic screening, as calculated using SCF minimal-Slater core orbitals with optimized exponents. These exact coulombic screening calculations include what Slater[32] calls both "inner" and "outer" shielding. Here we have chosen the α_A value so as to match the valence eigenvalues as nearly as possible. It is evident that the shape of the screening function of eq 12 is quite good. One-center core-valence exchange has been implicitly included in the screening parameter, α_A. Although such exchange is small, it does cause the $f(r_A)$ curve to fall off more slowly in the valence region than does the curve including only coulombic effects; at large distances, the $f(r_A)$ curve would therefore be expected to overemphasize core penetration effects. We therefore take Z_A^{eff} as $Z_A - N_c^A$ in molecular calculations for integrals of the form

$$\left\langle \chi_i^B \left| \frac{Z_A^{eff}}{r_A} \right| \chi_j^C \right\rangle \qquad (13)$$

when neither χ_i^B nor χ_j^C are centered on atom A. This has the added advantage of simplifying the calculation of these integrals, particularly in a Slater basis.

(3) The operator F depends on all other valence orbitals. Since use of pseudopotentials causes these orbitals to be indeterminate in the core region, this indeterminacy is introduced into the Fock operator. We shall skirt this problem rather than solve it. If the different valence orbitals are given sufficient freedom, it is very possible that some of the orbitals will collapse into the core region, not because of the lack of valence-core orthogonality, but to separate maximally the different valence electrons and thereby to minimize valence-valence electron repulsion. Since the purpose

Table III. Atomic Transition Energies Calculated in Minimal-Slater Bases. $s^2p^2(^3P) \rightarrow$ Indicated State (au)

Configuration	State	Full SCF	Core-orthogonal valence	Single-Slater valence	Exptl
			Carbon		
s^2p^2	^1D	0.066146	0.066146	0.066146	0.0464460
s^2p^2	^1S	0.165365	0.165365	0.165364	0.0986375
sp^3	^5S	0.098314	0.082389	0.064357	0.153709
sp^3	^3D	0.320326	0.304385	0.290989	0.292050
sp^3	^3P	0.386472	0.370531	0.357135	0.342893
sp^3	^3S	0.588863	0.573859	0.574012	0.482061
sp^3	^1D	0.565604	0.549940	0.545817	0.445965
sp^3	^1P	0.631750	0.616086	0.611962	0.546205
			Silicon		
s^2p^2	^1D	0.045808	0.045812	0.046173	0.0286995
s^2p^2	^1S	0.114503	0.114531	0.116783	0.0701414
sp^3	^5S	0.076945	0.078271	0.064609	
sp^3	^3D	0.233228	0.234477	0.224150	0.220513
sp^3	^3P	0.279055	0.280290	0.270863	
sp^3	^3S	0.426907	0.428220	0.422492	
sp^3	^1D	0.408177	0.409452	0.403091	
sp^3	^1P	0.453985	0.455267	0.449804	
			Germanium		
s^2p^2	^1D	0.045428	0.045431	0.045792	0.032465
s^2p^2	^1S	0.113562	0.113577	0.114481	0.074574
sp^3	^5S	0.069644	0.073527	0.064586	
sp^3	^3D	0.221236	0.225057	0.217781	0.272126
sp^3	^3P	0.266680	0.270488	0.263573	0.262787
sp^3	^3S	0.403236	0.407063	0.402609	
sp^3	^1D	0.388011	0.391825	0.386792	0.264684
sp^3	^1P	0.433410	0.437256	0.432584	0.252757

of our approach is to reduce the number of basis functions needed, we simply do not include functions localized principally in the core region, thereby making the problem of indeterminacy moot.

To summarize, we have suggested that a valence-only restricted pseudo-Fock operator may be written

$$F'\chi_i \equiv \left[T + U + \sum_{v}^{\text{valence}} (2J_v - K_v) + V\right]\chi_i = \epsilon_i\chi_i \tag{14}$$

where

$$V \equiv \sum_{A} \frac{f(r_A)}{r_A} + \sum_{c} |\phi_c\rangle(\epsilon_v - \epsilon_c)\langle\phi_c| \tag{15}$$

where

$$\left\langle \chi_i^B \left| \frac{f(r_A)}{r_A} \right| \chi_j^C \right\rangle = \left\langle \chi_i^B \left| \frac{(1 - e^{-\alpha_A r_A})N_c^A}{r_A} \right| \chi_j^C \right\rangle \tag{16}$$

$$\text{for A} = \text{B or A} = \text{C}$$

$$\left\langle \chi_i^B \left| \frac{f(r_A)}{r_A} \right| \chi_j^C \right\rangle = \left\langle \chi_i^B \left| \frac{N_c^A}{r_A} \right| \chi_j^C \right\rangle$$

$$\text{for A} \neq \text{B and A} \neq \text{C}$$

Application to Atoms. Atomic calculations were performed using Roothan's open-shell method[34] as modified by straightforward introduction of the potential of eq 15. For the atoms, we have taken the values $(\epsilon_v - \epsilon_c)$ for each orbital from minimal-basis-set STO calculations. As shown in Table II, we have optimized the values of α_A to four decimal places for the main-group elements from Li to Kr. These values of α_A were chosen so that the errors in the s and p eigenvalues relative to the full SCF calculation cancel. The α_A values were determined using atom-optimized exponents both for core-orthogonal valence wave functions obtained from the full SCF calculations as well as for noncore-orthogonal single-Slater functions, i.e., the basis functions corresponding only to valence orbitals. A comparison of these results with full SCF calculations is given in Table II. Since V^{PK} is clearly zero for the core-orthogonal functions, comparing these results with those of the full SCF calculation shows the errors introduced by the $f(r_A)$ term. Comparing core-orthogonal with noncore-orthogonal results shows the additional error introduced by V^{PK}.

As was discussed earlier, the difficulty in adapting pseudopotentials to the Hartree–Fock formalism lies in the treatment of electron repulsion. We treat this problem in *ad hoc* fashion by simply adjusting the α_A values to the particular basis set employed. Lower α_A values were required for the single-Slater valence orbitals than for the core-orthogonal functions. Since removal of the inner nodes of the valence functions increases the electronic repulsion between two electrons in a valence orbital, a counterbalancing decrease in the α_A values is necessary.

The computed transition energies from the ground states of C, Si, and Ge to a number of excited states are listed in Table III. The agreement of the full SCF calculation with those using core-orthogonal valence and single-Slater valence orbitals is quite good, indicating the effectiveness of the frozen-core approximation, the screened nuclear charge, and this adaption of the Phillips–Kleinman pseudopotential for atomic calculations. The agreement with experiment in both cases is only fair, except for triple-triplet transitions, for which the correlation energy of both states is about the same. This order of accuracy is not unexpected in any calculation that relys on the Hartree–Fock approximation.

Application to Molecules. In considering molecular systems, we treat the quantity $(\epsilon_v - \epsilon_c)$ in eq 15 somewhat differently than in the atomic case. The ϵ_c values are again taken from atomic calculations, but ϵ_v is taken as the lowest molecular valence eigenvalue computed in each SCF cycle. Use of different ϵ_v values for different orbitals was possible in the atomic case, where the Fock matrix is symmetry blocked; use of a common ϵ_v value is necessary in the molecular case, where symmetry is in general lacking, in order to assure that all the orbitals are eigenfunctions of the same operator and therefore orthogonal.

We have tested the method on the $^1\Sigma_g^+$ states of the diatomic molecules C_2, Si_2, and Ge_2. While the $^1\Sigma_g^+$ is the experimental ground state only of C_2 (Si_2 and Ge_2 have triplet ground states), this series seems to be an apt test for the method. Comparison of the same state for the three molecules indicates trends as atomic number increases; further-

Table IV. Valence Orbital Energies (au)

	C_2(STO/3G); R = 1.242 Å		Si_2(STO/3G); R = 2.115 Å		Si_2(uncontracted); R = 2.115 Å		Ge_2(STO/3G); R = 2.328 Å	
Orbital	Full SCF	NOCOR	Full SCF	NOCOR	Full SCF	NOCOR	Full SCF	NOCOR
				Occupied				
σ_g	−1.0574	−1.0304	−0.6508	−0.6550	−0.6947	−0.6591	−0.6082	−0.5925
σ_u	−0.5087	−0.4985	−0.4156	−0.4337	−0.4322	−0.4157	−0.3833	−0.4034
π_u	−0.4532	−0.4381	−0.2456	−0.2595	−0.2718	−0.2579	−0.2208	−0.2313
				Virtual				
$\sigma_g{}^*$	−0.0733	−0.0878	−0.0254	−0.0195	−0.0586	−0.0470	−0.0124	−0.0137
$\pi_g{}^*$	+0.2293	+0.1900	+0.0918	+0.0361	+0.0636	+0.0482	+0.0973	+0.0649
$\sigma_u{}^*$	+0.9591	+0.5181	+0.3503	+0.2901	+0.2458	+0.2189	+0.3359	+0.3736

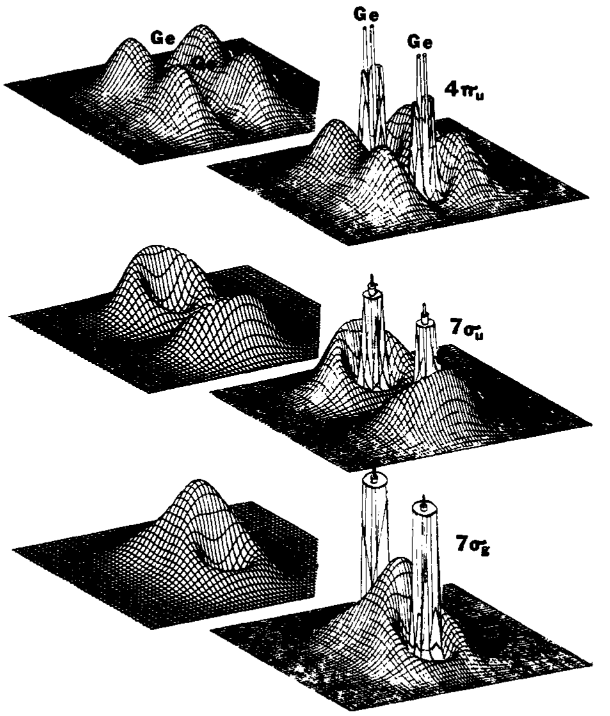

Figure 2. Valence-orbital electron-density plots of a cross section through the digermanium molecule, as calculated in an STO/3G minimal basis set (right-hand plots) and in the NOCOR approximation (left-hand plots). The electron density is plotted perpendicular to the geometric plane in which it is measured. The Ge–Ge distance is 2.328 Å.

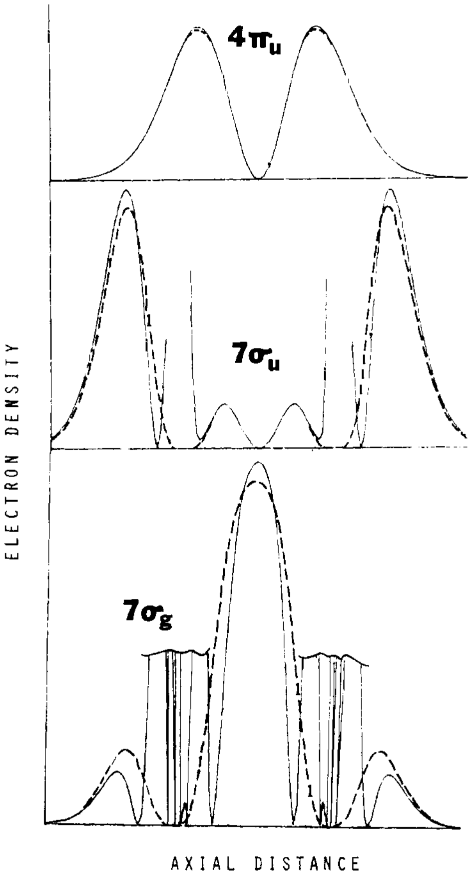

Figure 3. Plots showing the variation in electron density along the molecular axis for the two valence σ orbitals of the digermanium molecule and a similar plot (top) corresponding to the filled pair of π orbitals of this molecule measured along a line bisecting and perpendicular to its internuclear axis (Ge–Ge = 2.328 Å). The solid line in each plot corresponds to the STO/3G calculation and the dotted line to the NOCOR approximation. For the full calculation, the peaks in the core region are shown in detail only for the $7\sigma_g$ orbital and are truncated for both σ orbitals shown.

more, bonding in these molecules is in itself an interesting problem.[35] While comparison with experimental results is somewhat lacking for this series, we are more interested in comparison with full SCF results in the present work, since this latter agreement is the best we can hope to achieve. In this work, three Gaussian functions were contracted[36] in a least-squares fit to each Slater orbital of a minimal-Slater basis set for each molecule (*i.e.*, an STO/3G basis set was used). In order to test the effect of allowing greater freedom in the computation, we repeated the disilicon calculation in an uncontracted valence Gaussian basis, employing the same valence primitive functions as in the STO/3G calculation, but leaving their contribution to each molecular orbital unconstrained. In all cases, the core functions entering the pseudopotential were contracted to the core orbitals resulting from minimal-Slater atomic calculations. In order to simplify the integrals involved, the screening potential of eq 12 was fitted by a sum of six Gaussian functions. The α_A values obtained from minimal-basis atomic calculations (Table II) were used, based on the assumption that the core experiences relatively little change in going from an atom to a molecule (the frozen-core approximation). As may be seen from Table IV, the valence-orbital energies agree well with the equivalent (*i.e.*, STO/3G) full-SCF calculations.

Figure 2 shows a comparison of the electronic distribution of the NOCOR molecular orbitals with those of a full SCF calculation for the digermanium molecule. The two distributions are seen to be essentially identical outside the immediate region of the core. Similarly, the other molecules investigated in this study also exhibited electron-density distributions having the proper shape for the NOCOR orbitals outside of the core region. In the two lower plots of Figure 3, the electron-density profile along the molecular axis for the STO/3G NOCOR approximation (dotted line) is compared with the results for the full minimal-Slater calculation, and at the top of this figure, a similar comparison is made for the filled valence-shell π orbital as determined along a line bisecting and perpendicular to the internuclear axis. Note that for the NOCOR approximation the elec-

Table V. Calculated Equilibrium Bond Distances and Stretching Force Constants

Molecule	Bond distance, A			Force constant, mdyne/A		
	Full SCF	NOCOR	Exptl[a]	Full SCF	NOCOR	Exptl[a]
C_2(STO/3G)	1.323	1.289	1.2425[b]	13.28	14.26	12.25[b]
Si_2(STO/3G)	2.080	2.107		4.20	3.28	
Si_2(uncontracted)	2.116	2.033		3.16	3.12	
Ge_2(STO/3G)	2.087	2.352		4.78	3.28	

[a] The experimental ground states of Si_2 and Ge_2 are triplet states. [b] Reference 35.

tronic charge is, not surprisingly, drawn slightly in toward the core region for orbitals $7\sigma_g$ and $7\sigma_u$. Note also that this effect shows up indirectly for the plot given for orbitals $4\pi_u$ in that there is a slight diminution in the NOCOR peak intensities. Figures 2 and 3 demonstrate that a reasonably accurate description of the valence-shell electron densities is well within the grasp of the NOCOR method.

In computing potential curves, we have taken the combined core-core and nuclear-nuclear repulsion energy as

$$E_{\rm rep} = \sum_{A<B} \frac{(Z_A - N_c^A)(Z_B - N_c^B)}{R_{AB}} \qquad (17)$$

Inspection of Figure 1 suggests that the core potential falls off fast enough that this should be an excellent approximation at normal interatomic separations.

Equilibrium bond distances and force constants are reported in Table V. While the predicted bond distances and force constants are in good agreement for both C_2 and Si_2, the bond distance for Ge_2 is somewhat too long and the force constant too small. It is possible that the frozen-core approximation begins to break down as the core functions become more polarizable; a simple calculation[37] of core polarizabilities based on Slater screening constants gives values of 0.01, 0.34, and 5.40 au^3 for the cores of C, Si, and Ge, respectively. Other authors[38-40] have reached similar conclusions concerning the frozen-core approximation. However, to our knowledge, no other pseudopotential calculations have been performed by others on systems of complexity comparable to Ge_2, so that as yet we are not able to make any general conclusions in this regard. We are investigating other molecules containing third- and fourth-row atoms at this time and hope thereby to delineate the scope of applicability of the NOCOR procedure as outlined here (using one parameter per atom for the screening function) and to see if adjustments are needed to obtain more suitable valence-shell wave functions for such molecules.

Finally, to test the applicability of this method in predicting equilibrium bond angles and bending force constants, we have calculated these properties for PF_3. In this case we have also employed atom-optimized Gaussian functions[41-42] for the core potential, and again used an STO/3G basis set for the valence orbitals. The values we obtain, as well as equilibrium bond lengths, stretching force constants, and the barrier to inversion, are reported in Table VI. It may be seen from these results that the NOCOR method is in good agreement with both full SCF calculations and the experimental values, except for the inversion barrier. This again is not surprising, since inversion barriers are generally extremely sensitive to inadequacies in basis sets. Indeed, it appears[43] that large near-Hartree-Fock computations are needed to obtain a reasonably acceptable inversion barrier for ammonia, for example.

Table VI. PF_3 Molecular Properties

Property	Full SCF[a]	NOCOR	Exptl[b]
Equilibrium angle, deg	98.1	96.9	96.9 ± 0.7
Equilibrium bond length, A		1.472	1.563 ± 0.002
Symmetric stretching force constant, mdyn/A		6.60	6.23 ± 0.13
Symmetric bending force constant, mdyn A	2.59	2.07	1.96 ± 0.04
Barrier to inversion,[c] eV	5.82	8.97	

[a] L. J. Aarons, M. F. Guest, M. B. Hall, and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, 5, 643 (1973). [b] E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, 33, 460 (1970). [c] Corrected for zero-point vibration.

Conclusion

The NOCOR method promises to reduce greatly computation times relative to a full *ab initio* calculation, while retaining essentially the same level of accuracy. Systems containing heavy elements which cannot feasibly be treated in a full calculation may be routinely investigated using NOCOR. In contrast to (1) conventional SCF calculations, in which the time required increases according to the fourth power of the number of basis functions, and (2) valence-bond calculations which increase as *NN!* for *N* electrons, the computation time for a NOCOR calculation is a *constant* for a series of compounds in which one or more atoms are replaced by the successively heavier atoms from the same group of the periodic table. This relationship leads to large savings in computer time for molecules based on the heavier atoms. Thus, for example, only 2 min is needed to obtain the NOCOR wave function of digermanium as compared to 92 min for the equivalent full-core computation, using our Sigma-7 computer. We are currently applying the method to other areas of the periodic table, particularly the dihalogens and phosphorus halides, in an effort to determine further the extent of its applicability.

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A Thermochemical Study of the Hydrolysis of Urea by Urease

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Abstract: Hydrolysis products of the urea-urease system have been deduced from thermochemical measurements. Two distinct sets of products are found which depend upon the buffer used. Classical products (HCO_3^- and NH_4^+) are found in phosphate (pH 7.5 and 6.7) and maleate (pH 6.7) buffers. Ammonium carbamate in virtually quantitative yields is obtained in citrate (pH 6.7) and Tris (pH 7.5) buffers. The possible effect of these two sets of products on previous kinetic and thermodynamic studies is discussed in terms of buffer effects.

"Buffer effects" on the hydrolysis of urea catalyzed by crystalline urease (EC 3.5.1.5) are well known. These effects include the variation of the pH of maximum activity,[1] differing relative maximum activities,[1] varying susceptability to substrate inhibition,[2,3] and differences in activation energy data.[2,4] To date, the exact nature of the buffer contribution to these effects is not completely understood. Indeed, it is thought by some[5] that these effects arise from the method of enzyme preparation, or the presence of several isoenzymes.

This report concerns a thermochemical study of the hydrolysis products of urea. The results show that the product formed is dependent upon the buffer used, and this information is helpful in elucidating some of the above "buffer effects."

Theory

Heats of reaction may be determined calorimetrically by measuring the temperature change due to a chemical process. A knowledge of the moles of product formed (n_p) and the heat capacity of the system (k) yields ΔH via eq 1.

$$\Delta H = -\Delta T(k)/n_p \qquad (1)$$

For the hydrolysis of urea, there is sufficient thermochemical data available to calculate theoretical heats of reaction, at standard state ($\Delta H°$). Reactions 2-4 summarize the processes involved in forming the classical products in approximately neutral solution. Notably, reactions 3 and 4 are pH dependent.

$$H_2O(l) + urea(aq) \longrightarrow CO_2(aq) + 2NH_3(aq) \qquad (2)$$

$$H^+(aq) + CO_2(aq) + 2NH_3(aq) + H_2O(l) \longrightarrow 2NH_4^+(aq) + HCO_3^-(aq) \qquad (3)$$

$$H^+buffer(aq) \longrightarrow buffer(aq) + H^+(aq) \qquad (4)$$

From data on heats of formation,[6] the heat of reaction for process 2(ΔH_2) is found to be +7.29 kcal/mol urea. The heat of reaction of processes 3 and 4 ($\Delta H_{3,4}$) is given by eq 5. In this expression, K_1, K_2, and K_b

$$\Delta H_{3,4}(\text{kcal/mol urea}) = \frac{[H^+]K_1(\Delta H_{H_2CO_3} - \Delta H_{buffer}) + K_1K_2(\Delta H_{H_2CO_3} + \Delta H_{HCO_3^-} - 2\Delta H_{buffer})}{[H^+]^2 + [H^+]K_1 + K_1K_2} + \frac{2[H^+](\Delta H_{buffer} - \Delta H_{NH_4^+})}{[H^+] + K_w/K_b} \qquad (5)$$

represent the ionization constants for H_2CO_3, HCO_3^-, and NH_3, respectively. The ΔH values are for the ionization of a single proton from the subscripted species,[7] and it is assumed that there is always a sufficient amount of buffer present so that the pH change is virtually zero. Figure 1 illustrates the variation of the overall theoretical ΔH ($=\Delta H_2 + \Delta H_{3,4}$) with pH in phosphate buffer. This is a composite of three curves where the buffer systems are H_3PO_4-$H_2PO_4^-$, $H_2PO_4^-$-HPO_4^{2-}, and HPO_4^{2-}-PO_4^{3-}, and the appropriate ΔH_{buffer} was used for each. The overall curve represents the joining of these three segments.

The above discussion and results are valid as long as all of the carbon dioxide produced is capable of being aquated. If the solution is saturated with CO_2 and its hydrolysis products before the reaction is initiated, then $CO_2(aq)$ is replaced by $CO_2(g)$ in eq 2. The primary effect of this is to change ΔH_2 to a value of +11.98 kcal/mol urea, while the pH-dependent expression 5 loses the first term involving CO_2 and its hydrolysis products. The dashed curve in Figure 1 illustrates the results expected in this situation. If the solution *becomes saturated* with CO_2 during the course of the hydrolysis, the ΔH observed will lie somewhere between these two extremes.

In addition to the classical products, it has been shown that ammonium carbamate is a product of the hydrolysis of urea in alkaline, unbuffered solutions.[8,9] Reaction 6 sum-