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Ab initio effective potentials for use in molecular quantum mechanics*†

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We have investigated the method of effective potentials for replacing the core electrons in molecular calculations. The effective potential has been formulated in a way which simplifies computations while producing wave functions of *ab initio* quality. The effective potential is expressed in an analytic form which (i) represents the actual *ab initio* nonlocal potential (as defined by the matrix elements for a given basis set) and (ii) permits efficient computations of the effective-potential integrals (by incorporating the properties of Gaussian basis functions). To minimize the number of basis functions required in the molecular calculations, we define a new *ab initio* effective potential derived from modified Hartree-Fock valence orbitals whose core character has been removed. The effective-potential method as formulated becomes a very strong and reliable tool in attempting calculations on very large molecules. Applications to Li, Na, and K are presented.

I. INTRODUCTION

For many years chemists and physicists have realized that many of the chemical and physical properties of atoms are determined by only the outer few (valence) electrons. Indeed, the concept of the periodic table is derived from this idea. Thus, in describing the nature of the chemical bond, one need only focus his attention upon a few electrons for each atom so that, in a chemical sense, molecules involving Ra are no more complicated than those involving Mg. Unfortunately, in quantum-mechanical considerations, the electrons are indistinguishable and all must be considered. Treating Ra is therefore considerably more complicated than treating Mg. However, it was clear to early workers that Ra and Mg could both be described as simple two-electron problems by merely replacing the Rn and Ne cores, respectively, with an appropriate effective potential (EP).[1,2]

As was realized by these workers, the EP could not be just some simple electrostatic potential due to the core electrons. Rather, it must also incorporate the effects of the Pauli exclusion principle, leading to additional repulsive terms in the EP's. However, no unique solution exists for this problem. As a result, a number of approaches have been suggested and used. Some approaches are empirical and adjust the EP to match some experimental data.[1-3] Other approaches are theoretically based and adjust the EP to match the results of *ab initio* calculations.[4-10]

In this paper we present a theoretically based method which has evolved from an approach previously applied by Goddard, Kahn, and Melius[7-10] to some simple systems. The method has been formulated to yield *ab initio* quality wave functions for the valence electrons[11a] while remaining computationally simple and straightforward.

Various empirical and *ab initio* approaches to EP's are described in Sec. II. The general forms of EP's and methods for determining the potentials are presented in Sec. III. Section IV contains the specific EP's obtained for alkali-metal atoms.

II. *AB INITIO* EFFECTIVE POTENTIAL

In the Hartree-Fock (HF) approximation for, say, the Na atom, the ground-state wave function has the form

$$\Psi = \mathcal{A}(\Phi_{\text{core}}\phi_v X) \ , \tag{1}$$

where Φ_{core} is a product of (ten) spatial orbitals very similar to the orbitals of Na^+ and ϕ_v is the valence orbital (the one removed in ionizing to Na^+). (X is an appropriate product of spin functions.) To obtain the HF wave function we solve for the orbitals of (1) self-consistently, leading to variational equations of the form

$$H^{\text{HF}}\phi_i = \epsilon_i \phi_i \ , \tag{2}$$

where the one-electron HF Hamiltonian (for ϕ_v) is given by

$$H^{\text{HF}} = -\tfrac{1}{2}\nabla^2 - Z/r + 2J_\alpha - \hat{K}_\alpha \ , \tag{3a}$$

where $-\frac{1}{2}\nabla^2$ is the kinetic-energy term and $-Z/r$ is the nuclear attraction potential. The quantities J_α and K_α depend upon which orbital ϕ_i is used in (2). For the valence orbital J_α is equivalent to the classical Coulomb potential due to a charge density corresponding to the Φ_{core}. The exchange operator $\hat{K}_\alpha$ is an integral operator resulting from the antisymmetric form of the wave function (i.e., from the Pauli principle).

It will be important in our later analysis to note that the valence orbital in (1) is *not* determined uniquely by the variational principle. One can modify ϕ_v by mixing in an arbitrary amount of any core orbital (doubly occupied in Φ_{core}) without changing the energy. In order to obtain unique solutions for ϕ_v, one generally *requires* that ϕ_v be orthogonal to the other occupied orbitals. In this special case the variational equation for ϕ_v has the form (3a). Although this orthogonality restriction has the desired consequence of leading to a prescription for a unique valence orbital, there is no reason to consider the orthogonal valence orbital ϕ_v to have a special significance over any other combination of ϕ_v with the various core orbitals[11b]

$$\overline{\phi}_v = \phi_v - \sum_c \lambda_c \phi_c \ . \tag{3b}$$

[Of course, with a nonorthogonal orbital $\overline{\phi}_v$, the form of the variation Eq. (3a) is modified, with new potential terms in addition to $2J_\alpha - K_\alpha$.] We will find it useful below to use a representation $\overline{\phi}_v$ of the valence orbitals in which the λ_c in (3b) are chosen so that $\overline{\phi}_v$ has small amplitude in the region where the core orbitals are large.

For the excited states of Na, the wave functions are also given by (1) with nearly the same Φ_{core} so that only ϕ_v changes. Ignoring the slight changes in the core orbitals, the valence orbitals for the excited states will also satisfy Eq. (2). We would therefore expect that the core orbitals could be replaced by the effective potential

$$\hat{U}_\alpha^{\text{HF}} = 2J_\alpha - \hat{K}_\alpha \ . \tag{4}$$

For a molecule involving Na bonded to something else, we might also expect that the core orbitals of Na could be replaced by the $\hat{U}_\alpha^{\text{HF}}$ given in (4), just as for the atomic states.

The J_α in (4) can be expressed as a function of r. If U_α^{HF} could also be expressed as a function of r,

$$U_\alpha^{\text{EP}}(r) \ ,$$

we could merely replace the core on each atom with $U_\alpha^{\text{EP}}(r)$ and consider only the valence electrons in all further considerations. In this case the nonkinetic part of (3) can be combined into one function representing an effective potential

$$V_\alpha^{\text{EP}}(r) = -Z/r + U_\alpha^{\text{EP}}(r) \ , \tag{5a}$$

so that the total one-electron Hamiltonian (3) becomes

$$h = -\tfrac{1}{2}\nabla^2 + V_\alpha^{\text{EP}}(r) \ . \tag{5b}$$

Thus the HF theory provides a basic foundation for the use of EP's.

However, (4) does not allow us to forget about the core orbitals, since $\hat{K}_\alpha$ is an integral operator and, upon operating on a function ϕ_v, leads to terms involving integrals over products of ϕ_v with core orbitals. Thus, in order to replace the core orbitals by an effective potential of the form (5), we need to approximate somehow the effect of the exchange integral K_α. There are many ways of doing this, leading to a number of types of EP's.

A. Empirically adjusted potentials

The first work on effective potentials was by Hellmann[1] and Gombas,[2] who used a simple, repulsive potential of the form

$$U(r) = (A/r)e^{-2Kr} \ , \tag{6}$$

with A and K determined empirically so that the first few excitation energies [of (5)] match the experimental values. Since their work, more general forms of the potential in (6) have been used with fits to a larger number of experimental excitation energies.[3]

Since the spectrum of states using (6) is matched to the experimental spectrum, the potential (6) in some sense corrects for differences in correlation energies in the various states (see Table I). However, inclusion of correlation (i.e., superposition of configurations) effects involving ϕ_v invalidates the use of (2) and hence invalidates the use of (5) to solve for the excited states of a system, even one with only a single valence electron. Thus determining a generalized form of the potential (6) to fit the excitation energies of the atom does *not* imply that the wave functions and other properties are well described. The use of such atomic potentials in a molecule could lead to large errors in describing molecular binding

TABLE I. Comparison of the theoretical (*ab initio* Hartree-Fock) and experimental ionization potentials (V^I). All energies are in hartree atomic units.[a]

State	Ionization potential Theor(HF)[b]	 Expt	Error in V^I $V^I_{\text{Expt}} - V^I_{\text{Th}}$
Li 2*S*	0.1964	0.1981	0.0017
Li 2*P*	0.1287	0.1302	0.0015
Li 3*D*	0.0556	0.0556	0.0000
Na 3*S*	0.1819	0.1889	0.0070
Na 3*P*	0.1094	0.1116	0.0022
Na 3*D*	0.0557	0.0559	0.0002
K 4*S*	0.1478	0.1595	0.0117
K 4*P*	0.0955	0.1002	0.0047
K 3*D*	0.0566	0.0614	0.0048

[a] 1 hartree = 27.211 eV.

[b] The theoretical ionization potential is taken as the orbital energy of the valence orbital from an HF calculation.

energies (and *a fortiori* other properties) despite good atomic excitation energies.

B. Theoretically based potentials

A different approach to EP's was suggested by Phillips and Kleinman[4] (PK), who modified the HF equations (2) (for a one-valence-electron system) into the form

$$(-\tfrac{1}{2}\nabla^2 - Z/r + \hat{U}^{\mathrm{HF}} + \hat{U}^{\mathrm{PK}})\chi_v = \epsilon_v \chi_v \quad , \tag{7}$$

where χ_v differs from the HF valence orbital ϕ_v in that core orbitals are subtracted from ϕ_v as in (3b) in order to obtain a valence orbital with no large oscillations in the core region. With this transformation the total potential

$$V = -Z/r + \hat{U}^{\mathrm{HF}} + \hat{U}^{\mathrm{PK}} \tag{8}$$

is relatively weak. This work stimulated a great deal of theoretical analysis on the electronic properties of solids, since the weak potential in (8) permitted the atomic cores to be considered as a perturbation to the free-electron gas. Phillips and Kleinman showed that (7) leads to the same energy ϵ_v as (2) if $\hat{U}^{\mathrm{PK}}$ has the form

$$\hat{U}^{\mathrm{PK}} = \sum_c (\epsilon_V - \epsilon_c) | \phi_c \rangle \langle \phi_c | \quad . \tag{9}$$

In this viewpoint of the EP, $\hat{U}^{\mathrm{PK}}$ (called the pseudopotential) is a repulsive potential which plays the role of enforcing the Pauli principle, preventing χ_v from collapsing into the core. The $\hat{U}^{\mathrm{PK}}$ was generalized by Weeks and Rice[5,12] in order to account properly for the off-diagonal Lagrange multipliers necessarily present in the HF equations for open-shell systems. (A detailed discussion of these methods and others has been presented by Weeks, Hazi, and Rice[5] and by Kahn and Goddard.[9])

Although (7) and (2) are equivalent for the first state ϵ_v, they are *not* equivalent in general for the excited states. In addition, (7) is not unique since an infinite number of possible choices exist for $\hat{U}^{\mathrm{PK}}$, corresponding to all the ways of changing the amount of core character (ϕ_c) in ϕ_v to form χ_v,

$$\chi_v = \phi_v - \sum_c \lambda_c \phi_c \quad . \tag{10}$$

Furthermore, the effective potential in (9) is still an integral operator and hence is not as convenient as a local potential such as (6). To obtain an EP that is a function of r, one can let (9) operate on $\chi_v(r)$ and then divide by $\chi_v(r)$. (If χ_v has a node, this approach leads to a difficulty since the resulting potential has a singularity, forcing all the excited-state orbitals also to have a node at that point.) However, we still obtain an infinite number of such local potentials, each with its own spectrum of excited states.

C. GVB *ab initio* effective potential and minimum-kinetic-energy effective

Goddard included dominant correlation terms missing in the HF method by using a wave function corresponding to a generalization of the valence-bond-type wave function (denoted as GVB) in which the orbitals are solved for self-consistently.[13,14] With this approach the orbitals are given by a set of equations similar to (2)

$$H^{\mathrm{GVB}} \phi_i = \epsilon_i \phi_i \quad , \tag{11}$$

where H^{GVB} is similar to H^{HF} but contains a more complicated exchange term than $\hat{K}_\alpha$ (involving integral operators). A major difference is that the GVB method[14] (also called the G1 method[13]) leads to GVB valence orbitals that are *not* orthogonal to the core orbitals. In addition, these orbitals are smooth in the core region and are uniquely determined. This suggested using the GVB *ab initio* method on the atoms to determine the unique (smooth) orbital ϕ_v and then choosing the effective potential (called the GVB atomic EP or GAEP[7,9]) for replacing the core as

$$V^{\mathrm{GVB}}(r) = \frac{[\epsilon_i + (1/2)\nabla^2]\phi_v}{\phi_v} \quad . \tag{12}$$

This approach was applied by Kahn, Melius, and Goddard[8-10] to the ground and excited states of several small diatomic and triatomic molecules and was found to provide good quality wave functions and properties as well as energies.

While the GVB valence orbital ϕ_v^{GVB} is unique, a combination of occupied HF orbitals as in (3b) or (10) can be found that is similar to ϕ_v^{GVB}. Surratt and Goddard[15] found that if λ in (10) is determined to minimize the kinetic energy of χ_v, the resulting orbital χ_v^{MKE} is very close to the GVB orbital. The resulting minimum-kinetic-energy effective potentials (MKE EP's) are therefore similar to the GAEP's. Austin, Heine, and Sham[16] had previously suggested that the MKE EP would be a reasonable choice for defining a unique EP. Both of these potentials have been used for calculations on solids.[17,18] Since the potentials are weak, the crystal eigenfunctions are plane-wave-like and can be well described in terms of a linear combination of just a few plane waves, thereby reducing the computational effort (a very large number of plane waves would be required in the expansion of the usual HF orbitals).

D. Coreless Hartree-Fock effective potential

The above results indicate that one need not go to the GVB wave function to obtain an effective potential. The HF valence orbital can be used if one removes the condition that it be orthogonal to the core orbitals. One should next determine whether some choice other than MKE would lead to useful potentials. From considerations of the effective potentials obtained from different forms of ϕ_v [as in (3b)], we have concluded that the main consideration is that the λ_c of (3b) be chosen such that the resulting $\overline{\phi}_v$ is as small as possible throughout the entire region where the core orbitals are large. We will refer to the resulting orbital as the *coreless Hartree-Fock* (CHF) orbital since it has minimal amplitude in the core region. The resulting CHF orbital cannot be zero in the core region since it must have the form (3b). In addition, the CHF orbital will not in general be orthogonal to the core orbitals.

A major reason for using the CHF potential is computationally based.[19] In carrying out molecular calculations we expand each valence orbital in terms of a set of basis functions $\{\chi_\mu\}$ (e.g., Slater or Gaussian functions) of appropriate shape centered on the various atoms. In this case the differential equation (2) becomes a matrix equation

$$HC_i = \epsilon_i C_i \quad , \tag{13a}$$

where

$$H_{\mu\nu} = \langle \chi_\mu | \mathcal{H}^{\mathrm{HF}} | \chi_\nu \rangle \quad . \tag{13b}$$

The cost of computing the molecular eigenfunctions generally varies as the fourth power of the number of basis functions that must be included, and hence we wish to keep the size of this set to a minimum but without sacrificing accuracy.

For example, consider the K atom. With Gaussian basis functions, it requires about nine functions to obtain a good description of the valence 4*s* HF orbital (since it must contain 1*s*, 2*s*, and 3*s* character). By using instead the GVB or MKE description, the valence orbital is relatively smooth in the core region (see Fig. 1) and requires fewer functions (only about six) for a good description. Even though these GVB and MKE orbitals are relatively smooth, they do have a cusp at the nucleus and possess some wiggles at small r. To describe such cusps and wiggles requires basis functions in the core region. In order to minimize the basis-set requirements, we would like to suppress all unnecessary cusps and wiggles in the core region. This suggests starting with the HF valence orbital and mixing with it core orbitals

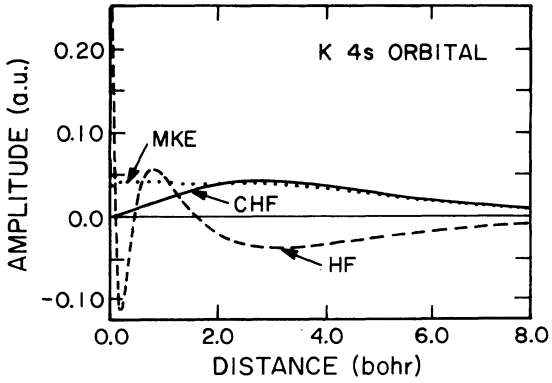

FIG. 1. Comparison of the K 4*s* orbitals obtained in the Hartree-Fock (HF), minimum kinetic energy (MKE), and coreless HF (CHF) descriptions.

$$\overline{\chi}_v = \chi_v - \sum_c \lambda_c \chi_c \quad , \tag{14}$$

with the requirement of minimizing the number of corelike basis functions needed to describe χ_v. Since each HF orbital satisfies the cusp condition at the nucleus,

$$\left(\frac{1}{\chi_v} \frac{d}{dr} \chi_v \right)_{r=0} = -\frac{Z}{l+1} \quad , \tag{15}$$

a cusp $[(d/dr)\chi_v \neq 0, \text{ for } r=0]$ and the concomitant corelike basis functions are avoided only if $\chi_v(0) = 0$. Thus we want the coefficients in (14) to be such that $\overline{\chi}_v(0) = 0$. One might then define the other conditions (if any) on the coefficients so that higher-order derivatives would also be zero at $r=0$. However, we found for Na that requiring the first two derivatives to be zero led to a function that becomes slightly negative for small r, changes sign at small r, and then becomes large and positive. This character near $r=0$ would tend to increase the size of the basis set.

We have instead formulated the CHF criteria that place conditions on the over-all shape of $\overline{\chi}_v$ rather than upon properties at one point. Namely, we choose the coefficients in (14) so as to obtain a best fit of $\overline{\chi}_v$ to an $n=3$ Slater orbital[20]

$$r^2 e^{-\zeta r} \quad .$$

[where $\zeta = (-2\epsilon)^{1/2}$]. This leads to a $\overline{\chi}_v$ that is smoothly decreasing in the core region, the desired property for reducing the size of the basis. As indicated in Fig. 1, χ_v^{CHF} goes to zero at the origin but has no other nodes in it. The corresponding EP can then be obtained, for example, by inverting the orbital [as in (12)]:

$$V^{\mathrm{CHF}}(r) = \frac{[\epsilon_v + (1/2)\nabla^2]\chi_v^{\mathrm{CHF}}}{\chi_v^{\mathrm{CHF}}} \quad . \tag{16}$$

The resulting CHF EP's for the alkali atoms are presented in Sec. IV.

The computational advantages of this smooth Hartree-Fock orbital are obvious. Since the new orbital has small amplitude throughout the core region, no tight basis functions (i.e., basis functions with high exponents) are required in the molecular calculations. In particular, one can use

Gaussian basis functions. Gaussian basis functions are advantageous because the one- and two-electron integrals can be evaluated analytically, thereby greatly reducing the computational time. These same properties of the Gaussian basis functions can also be used to evaluate the effective potential integrals analytically (see Sec. III B).

The usual difficulty with Gaussian basis functions has been their poor description of the sharp-cusp character of the orbital near the origin. Since Gaussians are flat at the origin, many tight Gaussian basis functions have been required to describe adequately the steep slope of the cusp (with the integral time growing as the number of basis functions to the fourth power). On the other hand, using the smooth CHF orbital, the orbital is flat at the origin and no such difficulty arises. As a result only valence-type basis functions are needed, leading to a significant decrease in the computational effort.

As an example, we compare in Table II the basis functions required for the HF and CHF descriptions of the K 4*s* valence orbital.[21] We see that both the HF and CHF orbitals use two valence-type basis functions ($\zeta_{\mathrm{HF}}=0.017$ vs $\zeta_{\mathrm{CHF}}=0.018$ and $\zeta_{\mathrm{HF}}=0.036$ vs $\zeta_{\mathrm{CHF}}=0.041$) as well as a somewhat tighter basis function ($\zeta_{\mathrm{HF}}=0.31$ vs $\zeta_{\mathrm{CHF}}=0.27$). However, while the CHF 4*s* orbital needs only these three basis functions, the HF 4*s* orbital needs six additional tight core basis functions to describe the oscillations in the core region and to provide comparable accuracy in the orbital energy.[22]

III. FORMATION OF EFFECTIVE POTENTIALS

A. General form of effective potential

Empirical methods of generating EP's have generally concentrated on fitting the energy spectrum of the atom. However, we are not interested in just the energy, but also we want to obtain many other properties for molecular systems. Thus we want the EP to be such that the whole wave function is accurately described, not just the energy.[23] Indeed, even to obtain good potential-energy curves, it is necessary that the various atomic orbitals have the right shape so that the interatomic overlaps (and other quantities related to bonding) behave properly with R. This suggests that the EP be chosen so that its *eigenfunctions* (not just its eigenvalues) are as close as possible to the eigenfunctions obtained with *ab initio* potentials.

In the self-consistent field approaches, such as HF [Eq. (2)] or GVB [Eq. (11)], each orbital (singly occupied) is an eigenfunction of a one-electron Hamiltonian which includes the effect of all the other orbitals (and includes exchange or nonlocal terms). That is, for each ϕ_i (e.g., χ_v^{MKE}, ϕ_v^{GVB}, χ_v^{CHF})

$$H_i\,\phi_i=\epsilon_i\phi_i \quad , \tag{17a}$$

$$H_i\equiv-\tfrac{1}{2}\nabla^2+\hat{V}_i \quad , \tag{17b}$$

where $\hat{V}_i$(e.g., $\hat{V}_i^{\mathrm{MKE}}$, $\hat{V}_i^{\mathrm{GVB}}$, $\hat{V}_i^{\mathrm{CHF}}$) is a nonlocal potential operator depending on the other orbitals.[24] Replacing $\hat{V}_i$ by the local operator $V_i(r)$,

$$V_i(r)=\frac{1}{\phi_i}\;\hat{V}_i\phi_i=\frac{[\epsilon_i+(1/2)\nabla^2]\,\phi_i}{\phi_i} \quad , \tag{18}$$

we obtain an effective potential which is equivalent to the nonlocal potential for that particular orbital. Solving for the eigenfunction of $H_i=T+V_i(R)$ then leads back to the original ϕ_i.

Let us now consider another electronic state of the system. Again, each orbital ϕ_j' is obtained from a one-electron Hamiltonian,

$$H_j'\phi_j'=\epsilon_j'\phi_j' \quad , \tag{19a}$$

$$H_j'\equiv-\tfrac{1}{2}\nabla^2+\hat{V}_j' \quad , \tag{19b}$$

for which one could obtain a new effective potential

$$V_j'(r)=\frac{[\epsilon_j'+(1/2)\nabla^2]\,\phi_j'}{\phi_j'} \quad . \tag{20}$$

In general, the V_j' obtained in (20) is not equal to the corresponding V_i of another state [say (18)] for the molecular system. In some cases, however, when V_i for orbital ϕ_i is used in place of V_j' in Eqs. (19), the new $\phi_j'^{\,\mathrm{EP}}$ and $\epsilon_j'^{\,\mathrm{EP}}$ will be very similar to the original ϕ_j' and ϵ_j'.[25]

TABLE II. Orbital exponents (ζ_i) and coefficients (c_i) to describe the K 4*s* HF and CHF orbitals in a Gaussian basis set (all functions are Gaussian orbitals).

HF[a]		CHF	
ζ_i	c_i	ζ_i	c_i
150 591	−0.000 01		
22 629.6	−0.000 04		
5 223.16	−0.000 19		
1 498.06	−0.000 76		
495.165	−0.002 53		
180.792	−0.006 81		
71.1940	−0.013 37		
29.3723	−0.010 81		
8.688 63	0.050 66		
3.463 82	0.090 76		
0.811307	−0.143 49		
0.312 555	−0.301 29	0.270 275	−0.215 71
0.035 668	0.701 02	0.040 528	+0.594 88
0.016 517	0.407 65	0.018 283	+0.518 10

[a] A. J. H. Wachters, J. Chem. Phys. 52, 1033 (1969).

To understand when this will happen, we need to consider more closely the form of the nonlocal potential operators $\hat{V}_l$ and $\hat{V}_l'$. Since $\hat{V}_l$ is nonlocal, it depends explicitly upon all the other orbitals of the system. Thus the effective-potential method will be appropriate only for those systems for which the other orbitals (i.e., the core orbitals) do not readjust significantly from one state to another. (We will refer to this as condition 1.) However, because of the exchange operator, we see that the potentials also depend upon the valence orbital

$$K_c(1)\phi_v(1)=\phi_c(1)\int d^3r_2\,\frac{\phi_c^*(2)\phi_v(2)}{r_{12}}\ .$$

Thus the two localized potentials will be similar only if the two (valence) orbitals are similar. Of course, the two orbitals cannot be similar everywhere, since they must be orthogonal to each other. But the exchange operator weights only that part of the valence orbital for which $\phi_c(2)\phi_v(2)/r_{12}$ is large and hence only the region near the core. Therefore, as long as the excited-state orbital has the same shape in the core region as the valence orbital,[26] one would expect the local potential for the excited-state orbital to be similar to the local potential for the valence orbital. (We will refer to this as condition 2.)

As an example we consider the Li atom, with three electrons. In particular, we will examine the GVB representation, for which each of the orbitals is uniquely defined. The excited states of the Li atom represent the excitation of the outer or valence electron, while the two inner electrons remain essentially the same as the ground state. Therefore condition 1 is satisfied. However, in order to replace the core by an effective potential, we also require that the valence orbital for each excited state have the same shape in the core region. To determine if this is reasonable, we have plotted in Fig. 2 the valence orbitals for several of the low-lying states of the Li atom. We see that the $2\,{}^2P$ orbital is very different from the $2\,{}^2S$ orbital in the region of the core and thus we would *not* expect the effective potentials for these two states to be similar. On the other hand, the $3\,{}^2S$ orbital has essentially the same behavior as the $2\,{}^2S$ orbital in the core region[27] (within a scaling factor), as do the higher ${}^2S$ orbitals. Thus for the ${}^2S$ states we would expect the effective potentials to be similar (condition 2 is satisfied). Likewise, all the ${}^2P$ states can be represented by the same effective potential, and so on for the other (bound) angular-momentum states. We would therefore expect that the core orbitals can be replaced by an effective potential of the form

$$V_{\rm eff}=\sum_{l=0}^{\infty} V_l(r)\,|l\rangle\langle l|\ , \qquad (21)$$

where $|l\rangle\langle l|$ denotes the sum over m of $|lm\rangle\langle lm|$, where $|lm\rangle$ denotes the spherical harmonics and the projection operator $\langle lm|$ involves integration over angular coordinates only. While there is a different potential for each angular momentum, one local potential $V_l(r)$ is sufficient for describing the various (bound) excited states of the same angular momentum.

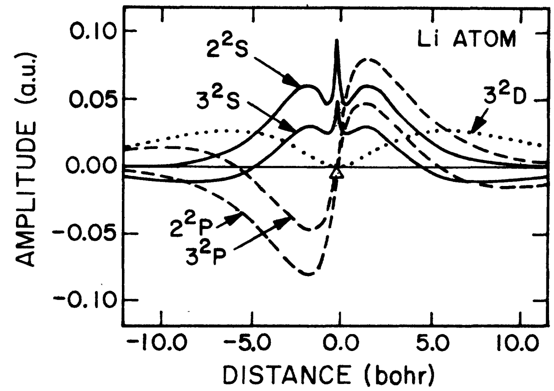

FIG. 2. Valence orbital for various excited states of Li (all for self-consistent GVB wave functions).

The $V_s(r)$, $V_p(r)$, and $V_d(r)$ obtained for the Li atom (excluding $-Z_n/r$) are shown in Fig. 3. While V_s is quite different from V_p and V_d, we see that V_p and V_d are quite similar. This results from the p and d orbitals having similar character in the core region (zero amplitude at the origin but no other nodes), since there are no core orbitals of these symmetries, while the valence s orbital is greatly affected by the presence of core orbitals with s symmetry. The higher-angular-momentum orbitals should be very similar to the d orbital in the core region, yielding V_l's essentially equivalent to $V_d \approx V_p$. From such

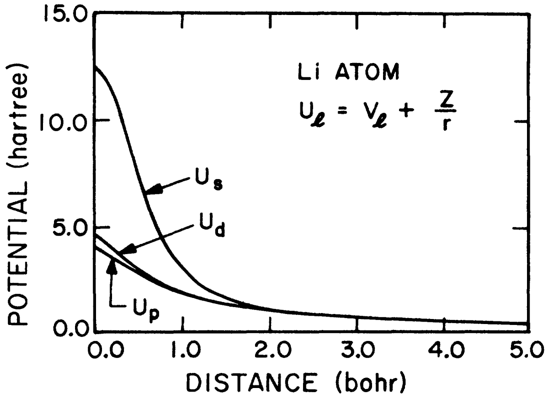

FIG. 3. U_s, U_p, and U_d local potentials for Li atom obtained from the GVB orbitals.

considerations we expect that for angular momenta l greater than the maximum angular momentum λ involved in the core ($\lambda = 0$ for Li, $\lambda = 1$ for Na and K) the V_l should be approximately equal,

$$V_l \approx V_{\lambda+1} \quad \text{for } l > \lambda \ .$$

In this case (21) becomes

$$V_{\text{eff}} = V_{\lambda+1}(r) + \sum_{l=0}^{\lambda} \Delta V_l(r) | l \rangle \langle l | \ , \tag{22}$$

where $\Delta V_l \equiv V_l - V_{\lambda+1}$.

Thus far we have considered the electron moving in a spherically symmetric potential of the atom, obtaining an effective potential which is valid for the spherically symmetric atomic case. We must now consider whether the potential is still valid for an electron moving in a molecular system. To proceed, we can expand the electronic orbital in terms of the spherical harmonics of the atom and use the potential as defined in (22). However, for the potential to be accurate, the radial part of the orbital for each angular term must have the same character near the core as did the corresponding atomic radial function. For most molecules this is indeed the case. That is, near the atom, the wave function can be expressed quite well as a linear combination of the lower-lying states of that atom.[28]

The effective-potential approximation will break down if the cores (which are taken to be frozen) are greatly perturbed. Furthermore, the effective-potential approximation will not be accurate if the valence electron is located within a portion of the core region (for example, by bringing a highly charged ion into close proximity with the core). The reason is that the local effective potential obtained in (18) represents the actual nonlocal potential only in a global sense (averaging over the region of the core) and is not valid in a pointwise sense. These are not serious problems, however, if care is taken when applying effective potentials to molecular systems. In general, therefore, we find that effective potentials defined as in Eq. (22) can be used in a wide range of molecular wave functions yielding results that should be in close agreement with the *ab initio* results.

B. Analytic form of effective potential

In order for effective potentials to be utilized advantageously in SCF calculations, the integrals involving these potentials must be evaluated efficiently. Therefore, the effective potentials must have a simple form yet sufficient flexibility to reproduce the effect of the replaced electrons. It was shown in Sec. IIIA that effective potentials can correctly represent the effect of the core electrons in molecular systems if the EP has the form

$$V_{\text{eff}} = \sum_{l=0}^{\infty} V_l(r) | l \rangle \langle l | \ , \tag{21}$$

where V_l is a function only of r [i.e., V_{eff} is a local potential not depending explicitly (as an integral function) on the core orbitals]. We have further found that the effective potential can be put into the form

$$V_{\text{eff}} = V_{\lambda+1}(r) + \sum_{l=0}^{\lambda} \Delta V_l(r) | l \rangle \langle l | \ , \tag{22}$$

where $\Delta V_l = V_l - V_{\lambda+1}$. We now wish to find a simple form for V_{eff} as defined in Eq. (22).

In evaluating the integrals, we will take the basis functions to be Gaussians. The well-known advantages of Gaussian functions for evaluating multicenter molecular integrals can also be used in evaluating the effective-potential integrals. [As previously mentioned, by using the CHF effective potential the major drawback of Gaussians (i.e., the need for many basis functions) has been eliminated.]

The types of molecular integrals that must be evaluated are

$$\langle \chi_a | U_a | \chi_a \rangle \ ,$$

$$\langle \chi_b | U_a | \chi_a \rangle \ ,$$

$$\langle \chi_b | U_a | \chi_c \rangle \ ,$$

where the a, b, and c indicate the origin used for the basis function (χ) or potential ($U = V_l$ or ΔV_l). Substituting the Gaussian form for the basis functions then leads to integrals of the form

$$\int_0^\infty U(r) r^n e^{-\zeta r^2} r^2 \, dr \ , \tag{23a}$$

$$\int_0^\infty U(r) r^n e^{-\zeta r^2} M_l(ar) r^2 \, dr \ , \tag{23b}$$

$$\int_0^\infty U(r) r^n e^{-\zeta r^2} M_{l_1}(ar) M_{l_2}(br) r^2 \, dr \ , \tag{23c}$$

where the M_l's are modified spherical Bessel functions. Since the V_l depend only on the scalar coordinate r, the angular integrations in (23) have been carried out explicitly. One could evaluate these integrals by direct numerical integration. However, we found that this procedure leads to computation times comparable to that for two-electron molecular integrals,[9] thereby partly defeating the purpose of using effective potentials.

Instead, we will use an expansion of the potential $U(r)$ in terms of a standard set of convenient functions of r, $\{\mu_k(r)\}$ and we will evaluate each of the integrals analytically. The expansion functions

$\mu_k(r)$ must be chosen both (i) to allow accurate expansions of the $U_a(r)$ and (ii) to allow for simple analytic forms for the integrals in (23). From the form of (23) we see that an expansion function of the form

$$\mu_k(r) = r^{n_k} e^{-\zeta_k r^2} \tag{24a}$$

can be combined with the $r^n e^{-\zeta r^2}$ parts of the integrand to yield a new integral of the same form as (23) but with the $U(r)$ deleted. Thus expanding the potential as

$$U(r) = \sum_k c_k \mu_k(r) \tag{24b}$$

and using (24) leads to integrals that are essentially no more difficult to evaluate than the overlap $[U(r) \equiv 1]$ and the nuclear potential $[U(r) \equiv -Z/r]$ integrals. These integrals can be readily expressed in analytic form.[29]

To determine what type of terms are required in (24), we multiply the effective potential by r, generating the negative of what is called the (radially dependent) effective charge

$$V_{\text{eff}}(r) = -Z_{\text{eff}}(r)/r \ . \tag{25}$$

At the origin $Z_{\text{eff}}(0)$ will equal Z_n. Letting Z_{core} represent the number of electrons that are replaced by the potential, $Z_{\text{eff}}(\infty)$ equals the difference between the nuclear charge and $Z_{\text{core}}[Z_{\text{eff}}(\infty) = Z_n - Z_{\text{core}}]$. Defining $\Delta Z_{\text{eff}}(r)$ as the difference between effective charge at infinity and the actual effective charge, i.e.,

$$\Delta Z_{\text{eff}}(r) = Z_{\text{eff}}(\infty) - Z_{\text{eff}}(r) \ , \tag{26}$$

we see that ΔZ represents the modification of the potential (by the core electrons) from that of a hydrogenic system [with charge $Z_{\text{eff}}(\infty)$].

As an example, we consider the V_s potential of the Li atom. The effective potential obtained from the MKE HF Li 2^2S orbital (which has essentially the same behavior as the GVB orbital) is shown in Fig. 4(a). In Fig. 4(b) we show ΔZ_{eff} for the MKE Li $2s$ orbital. The function $\Delta Z_{\text{eff}}(r)$ is localized in the region of the core orbitals. It rises smoothly from a value of $-Z_{\text{core}}$ at the origin to a maximum at ~0.5 bohr and then falls off quickly to zero (by $R \approx 3a_0$). The positive region of the potential represents the repulsive character of the effective potential (due primarily to the Pauli principle), keeping the valence orbital of Li from collapsing into the core. From Fig. 4(b) we would expect that terms of the type in Eq. (24) with $n_k = -1$ and 0 could readily reproduce the shape of ΔZ_{eff}.

We now consider the new V_s effective potential for the Li atom resulting from the coreless Hartree-Fock orbital (CHF). This new potential is plotted in Fig. 4(b). Since this new orbital has zero amplitude at the origin, the effective potential must behave as r^{-2} for small r. [It is this repulsive singularity which prevents the lowest (nodeless) solution of the potential from collapsing into the core.] Thus we need to include terms in Eq. (24) with $n_k = -2$.

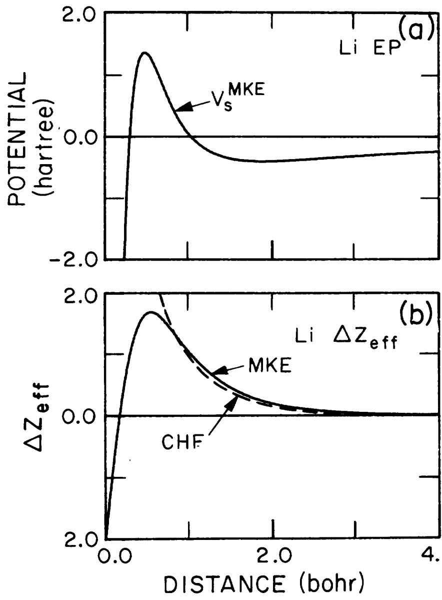

FIG. 4. (a) MKE V_s effective potential for Li atom, (b) the resulting $\Delta Z_{\text{eff}}^{\text{MKE}}$ and the corresponding $\Delta Z_{\text{eff}}^{\text{CHF}}$ for the CHF V_s local potential of Li.

In conclusion, therefore, we see that one can express an arbitrary EP in the form given in Eq. (24) using only terms with $n_k = 0$, -1, or -2. Methods to determine values of the variables c_k and ζ_k for each term will be discussed in Sec. III C.

C. Methods for obtaining effective potentials

In order to use effective potentials, we need a method for obtaining an analytic form for the EP correctly representing the effect of the nonlocal potential due to the core electrons.

One method would be to obtain the potential $V(r)$ by inverting the orbital,[7] as defined in Eq. (18). One can then fit the potential[8,9] by "least squares" with the form given in Eq. (24), optimizing the exponents and the coefficients. By adding a sufficient number of terms, one can obtain a fit to whatever degree of accuracy is desired.

While this approach is straightforward, several problems arise. For instance, how accurate does the fit need to be (that is, how many terms are needed)? This problem is made more complex when one realizes that the orbital used in the inversion [see Eq. (18)] is not exact but usually is an approximation expressed as an expansion in terms of some basis set. Therefore, the potential to which we would fit is itself only an approximation. Furthermore, the potential for one state of the system (e.g., Li $2\,^2S$) is only an approximation for another state of the system (e.g., Li $3\,^2S$). We might prefer to determine, say, V_s of Li to yield simultaneously a good fit for both the $2\,^2S$ and $3\,^2S$ states.

Additional problems can arise in this method from the over-all shape of the orbital used in Eq. (18). The orbital must be nodeless (except at $r=0$) to prevent singularities from arising in the potential. Also, using this method effective potentials can be obtained straightforwardly only for those systems which support a bound state, since we use the variational principle to obtain the orbital to be inverted. Thus, for example, one could not obtain a complete EP to replace the F^- ion since the F^- ^3S, $^{1,3}P$, etc., states do not exist.

To circumvent these problems, we have developed an alternative method for obtaining effective potentials. We require the local potential as given in Eq. (24) to reproduce the same matrix elements as those obtained from the original, nonlocal potential.[30] That is, we want $V_{\rm eff}$ to be such that

$$\langle \chi_\mu | V_{\rm eff} | \chi_\nu \rangle = \langle \chi_\mu | \hat{V} | \chi_\nu \rangle \ . \tag{27}$$

However, a local operator $V_l(r)$ cannot be equivalent to a nonlocal operator $\hat{V}_l$, and (27) cannot simultaneously be satisfied for all μ and ν. Thus we require (27) to be satisfied in a least-squares sense.

A method which makes direct use of this point is to choose the basis functions χ_ν to be the valence orbital(s) for some molecular system containing the frozen core. That is, we define $V_{\rm eff}$ to be

$$\langle \chi_\mu | V_{\rm eff} | \phi_v \rangle \simeq \langle \chi_\mu | \hat{V} | \phi_v \rangle \tag{28a}$$

$$= \langle \chi_\mu | \epsilon_v - T | \phi_v \rangle \ , \tag{28b}$$

where the χ_μ are chosen to span the space of the valence orbital. An immediate connection is seen between Eqs. (28b) and (18). However, since the inverse of ϕ_v is not required, it is permissible for ϕ_v to have nodes in it. Also, we can include other valence orbitals in Eq. (28a) [fitting then two or more columns of (28b)], permitting one to obtain the best EP satisfying both Eqs. (18) and (20). For systems which do not have bound states, one can still use Eq. (27) defined over basis functions.

By defining the effective potential as in (27), any new electronic orbital we obtain by solving (5b) using the EP will experience the correct field due to the core electrons (if the orbital is expressed in the same basis set as that used in fitting the matrix elements). Thus we no longer find it necessary to go through an intermediate stage of evaluating $V_{\rm eff}(r)$ as a function of r [as is implied from Eq. (18)]. The extent to which we can reproduce the nonlocal matrix elements by the EP matrix elements provides a *test of confidence* which can be applied to any calculations that would be based on that EP.

IV. EFFECTIVE POTENTIALS FOR THE ALKALI-METAL ATOMS

In this section we present examples of *ab initio* effective potentials which have been obtained for Li, Na, and K. The potentials were obtained using methods described in Sec. III. The alkali-metal atoms (Li, Na, K, etc.) contain a single-valence electron with a completely filled inner core of electrons (isoelectronic with the inert gases).

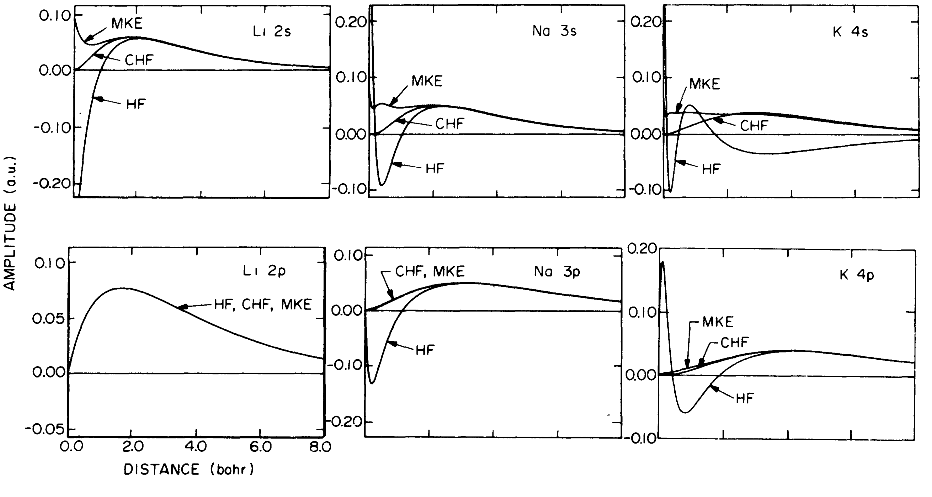

FIG. 5. Various HF, MKE, and CHF orbitals of Li, Na, and K.

The excited states of the atom represent a one-electron excitation of the valence orbital with the core orbitals remaining essentially unchanged. Therefore, the alkali atoms represent the ideal system for using effective potentials.

We present here results for two different effective potentials for the alkali atoms: (a) the EP obtained from the minimum-kinetic-energy Hartree-Fock orbital (MKE) [or from the nearly equivalent GVB orbital (GAEP)]; (b) the EP obtained from the newly defined coreless Hartree-Fock orbital (CHF). Plots of these various orbitals for Li, Na, and K are shown in Fig. 5 and compared with the HF orbitals.

We see that the amplitude outside the core is essentially the same for the HF, MKE, and CHF orbitals. However, the HF orbital has large oscillations and a significant amplitude in the core region. Likewise, the MKE orbital, though it is flat in the core region, still has wiggles in it and for the *s* orbital has a cusp at the origin. Therefore, both types of orbitals require tight basis functions. On the other hand, the CHF is smooth, having no wiggles in it.

To evaluate the EP's, Eq. (28) was used with ϕ_v representing the MKE or CHF orbital. The basis functions χ_μ were taken to be the same basis functions that were used in the solution of ϕ_v. Since the matrix elements for the most diffuse basis functions represent integration over the

TABLE III. Expansion terms for the CHF effective potentials.[a, b]

Potential	c_i	n_i	ξ_i
Li V_{S-D}	2.5378	−2	1.9088
	1.1097	0	0.9470
	0.3527	0	0.4905
	0.008 94	0	0.098 25
Li V_{P-D}	−0.1261	0	1.0147
	−0.1901	0	13.1143
	−0.2393	0	3.0810
Li V_D	−1.0	−1	0.0
	0.4296	−1	11.0026
	−2.4256	−1	1.5083
	2.0262	0	4.3868
	2.5342	0	1.7530
	−0.033 89	0	0.7159
Na V_{S-D}	5.8539	−2	1.3940
	29.4418	0	28.4200
	1.5541	0	0.6150
	0.006 67	0	0.0762
Na V_{P-D}	51.5653	−2	3.9264
	−46.9069	−2	1.7704
	87.5679	0	2.8630
	16.1439	0	1.5166
	0.3582	0	0.3031
Na V_D	−1.0	−1	0.0
	1.1004	−1	12.2245
	−11.0951	−1	1.3859
	9.3093	0	4.2010
	10.2369	0	1.7972
	−0.0220	0	0.2280
K V_{S-D}	8.2055	−2	0.3538
	0.5086	−2	0.0846
	−0.7927	0	1.0910
K V_{P-D}	6.8315	−2	0.4676
	0.2874	0	0.1496
	1.1498	0	0.4673
K V_D	−1.0	−1	0.0
	−4.4701	−1	0.6990
	−0.2924	−1	0.2042
	−0.1675	0	0.3325

[a] $V_l = \sum c_i r^{n_i} \exp(-\xi_i r^2)$.

[b] $V_S = V_{S-D} + V_D$; $V_P = V_{P-D} + V_D$.

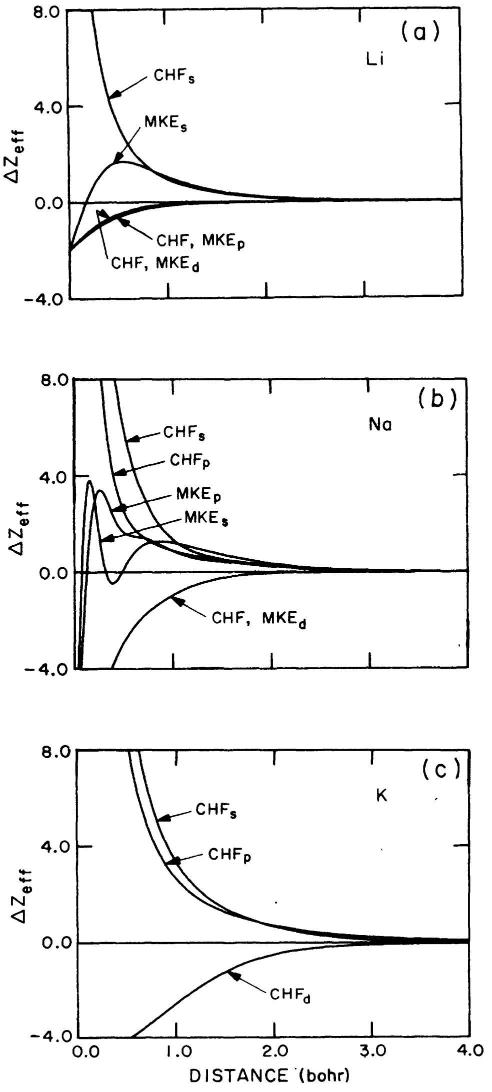

FIG. 6. Various ΔZ_{eff}'s for (a) Li, (b) Na, and (c) K, where $\Delta Z_{eff} = Z_{eff}(\infty) - Z_{eff}(r)$ [$Z_{eff}(\infty) = 1$].

entire potential,[31] we wanted these matrix elements to be very accurate. Therefore, a weighting of the matrix elements proportional to the inverse of the orbital exponent was used. Since calculations using the CHF EP will not use tight corelike basis functions (even if allowed to), we deleted such functions in fitting the potential.

The resulting EP's are smoothly varying functions. Therefore, very few terms are needed to express the potential. We find that the EP's obtained from these fits do not, in general, possess the exact form of the potential near the origin (e.g., $-Z_N/r$ for the MKE orbital), since the basis functions and valence orbital do not weight this region. However, such behavior near the origin is not important, since use of the EP to obtain matrix elements for molecular or atomic calculations will in turn also not weight these regions.

After performing the least-squares fit of the matrix elements, we obtain effective potentials for the various atoms. The ΔZ_{eff}'s for these potentials are shown in Fig. 6. The expansion terms for each of the EP's are given in Table III.

In general, we see that if the valence orbital has the same symmetry as one of the core orbitals, then the EP contains some repulsive character in the core region to prevent the valence orbital from collapsing into the core. For the CHF orbitals the repulsive character is represented by the singularity at the origin. The MKE EP's, on the other hand, are proportional to $-A/r$ ($A > 0$) near the origin.[32]

Using these EP's we have determined a set of optimized (Gaussian) basis functions for each atom. The basis sets were chosen to provide an accuracy in the energy to within 10^{-4} hartree ($\sim 3\times10^{-3}$ eV or $\sim 6\times10^{-2}$ kcal). The resulting basis sets (for CHF) are given in Table IV.

From Table IV we see that the larger atoms (e.g., K) require fewer basis functions than the small ones (e.g., Li). This is in direct contrast with the case of the orthogonal HF orbitals, where the number of basis functions required grows very quickly with the size of the atom. Thus the CHF effective potential provides a significant reduction in computation of the integrals while still providing *ab initio* quality.

V. SUMMARY

The justification for using effective potentials is to simplify the computational efforts required in solving for the electronic wave functions of large polyatomic molecules or solids. Toward this end we have developed the *ab initio* effective-potential method to provide reliable yet computationally efficient results. We have defined a new type of effective potential (CHF EP) derived from the newly defined CHF orbital. Since the CHF orbital does not contain core character, no tight basis functions are necessary in the calculations. To further simplify the computational efforts, we express the effective potential in an analytic form which permits rapid evaluation of the potential integrals over Gaussian basis functions. To ensure reliability in the EP calculations, we derive the local EP directly from the matrix elements of the actual *ab initio* nonlocal potential defined over a given set of basis functions. The extent of the fit between the EP elements and the nonlocal potential matrix elements provides a test of the reliability we can expect from the use of similar EP matrix elements in molecular calculations. Furthermore, by using the matrix-fit method for defining the EP's, we can obtain EP's for systems which have

TABLE IV. Gaussian basis sets for CHF orbitals (all quantities in Hartree atomic units).

Orbital	Exponent ζ_i	Coefficient c_i	ΔE[a]
Li 2*s*	2.893 79	−0.018 33	0.000 04
	0.618 15	−0.103 55	
	0.073 85	0.564 43	
	0.028 17	0.515 44	
Li 2*p*[b]	2.697	0.011 05	0.000 02
	0.535	0.059 75	
	0.147	0.231 26	
	0.0528	0.508 62	
	0.020 14	0.366 86	
Li 3*d*[b]	0.075 69	0.117 67	0.000 06
	0.022 60	0.496 39	
	0.008 30	0.526 00	
Na 3*s*	1.229 99	−0.035 46	0.000 02
	0.451 96	−0.113 38	
	0.057 80	0.673 83	
	0.021 91	0.415 26	
Na 3*p*	1.243 76	−0.007 72	0.000 03
	0.108 41	0.117 49	
	0.046 19	0.475 86	
	0.017 69	0.507 38	
Na 3*d*[b]	0.076 77	0.108 44	0.000 07
	0.022 45	0.518 79	
	0.008 25	0.529 22	
K 4*s*	0.270 28	−0.215 71	0.000 05
	0.040 53	0.594 88	
	0.018 28	0.518 10	
K 4*p*	0.442 96	−0.026 45	0.000 04
	0.038 88	0.500 49	
	0.014 39	0.574 13	
K 3*d*[b]	0.103 66	0.106 43	0.000 17
	0.024 85	0.524 83	
	0.008 49	0.545 88	

[a] ΔE is the difference between the orbital energy for the given basis set and the orbital energy for a very large basis set.

[b] The Li 2*p*, Li 3*d*, Na 3*d*, and K 3*d* HF orbitals are unique (CHF = HF).

no bound states (e.g., the ^3S and $^{1,3}P$ states of Cl^{-1}). In fact, using the matrix fit we can obtain EP's representing the potential an electron sees due to a molecular core such as a CO ligand in a metal complex. The essential requirement is that the electronic molecular core (being replaced) can be taken as frozen (i.e., having the same form for the various molecules, complexes, or excited states of interest).

Thus, using the methods developed in this paper, one should be able to use the effective-potential method as a reliable tool for calculations of large molecular systems.

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§Contribution No. 4763.

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[11a] When we discuss electrons, we are referring to the orbitals as obtained from an independent-particle–type wave function, such as obtained from the Hartree-Fock (HF) or generalized valence bond (GVB) method (see Ref. 14). Each electron is described by an orbital which represents the state of an electron moving in the average field due to the other electrons. The electrons are indistinguishable; it is actually the orbitals which are distinguished.

[11b] In evaluating properties of the wave function one must start with the basic form of the wave function (1). Thus using a nonorthogonal valence orbital (3b) in (1) for the lithium atom leads to the expression $\langle P\rangle = [\langle 1s|p|1s\rangle (2-S^2) + (v|p|v) - 2S\langle 1s|p|v\rangle]/(1-S^2)]$ for the expectation value of a one-electron operator $P=\sum_i p(i)$, where $S=\langle 1s|v\rangle$ is the overlap between the valence and core orbitals. Alternatively, one can orthogonalize the final valence orbital to the core orbital and use the usual expression $\langle P\rangle = 2\langle 1s|p|1s\rangle + \langle\bar{v}|p|\bar{v}\rangle$, where $\bar{v}$ is the orthogonalized orbital.

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[19] If the sole purpose of EP's were just to reduce the number of electrons, then little would have been gained, since one could have carried out "frozen-core" calculations instead. The cores are replaced by adding the matrix elements $\langle\mu|2J_{\mathrm{core}}-K_{\mathrm{core}}|\nu\rangle$ to the one-electron potential-energy terms, $\langle\mu|\sum_a(-Z_a/r_a)|\nu\rangle$.

[20] One should note that the new orbital is not equivalent to a Slater orbital, since it is restricted to be a linear combination of the HF valence and core orbitals as in (10). A weighting factor of r^{-2} is used in order to emphasize the fit in the core region.

[21] The basis set used for the HF orbital of K is from A. J. H. Wachters [J. Chem. Phys. 52, 1033 (1969)]. The five tightest functions are not really necessary unless a good cusp description is required.

[22] Using a very large basis rather than the three in Table II leads to a drop in the CHF orbital energy of 0.000 05 hartree (see Table IV), which can be taken as the basis set error for the CHF three-function basis. The HF results quoted in Table II are expected to have a comparable basis-set error since they are comparable in the valence region.

[23] Since the EP wave function should be very similar to the *ab initio* wave function, we expect the properties of the EP wave function (not just the energy) to be close to the properties of the SCF wave function.

[24] In addition to the exchange operator, $\hat{V}_i$ also contains projection operators onto the core orbitals. As a result, the matrix elements depend on the overlap of the valence orbital with the core.

[25] If ϕ_i' represents an excited state of the system, then we require that $\phi_i'^{\,\mathrm{EP}}$ be restricted to the space orthogonal to ϕ_i. For HF orbitals, special care must be taken. The orbitals ϕ_i and ϕ_i' are not unique [Eq. (10)]. Therefore the V_i and V_i' of Eqs. (18) and (20) are not uniquely defined, since they each replace the nonlocal projection operators which project away any arbitrary amount of core character. However, by requiring ϕ_i' to be or-

thogonal to ϕ_i, we can then compare $\phi_i'^{\,\mathrm{EP}}$ directly to ϕ_i'.

[26] The orbitals may differ by a normalization factor since the Hamiltonian equation is homogeneous in ϕ.

[27] This should be expected since a nodeless $3\,^2S$ orbital must mix in $2s$ character in order to be orthogonal to the valence $2s$ orbital.

[28] See, for example, C. F. Melius and W. A. Goddard III, J. Chem. Phys. 56, 3348 (1972).

[29] The resulting integrals [Eq. (23)] can be expressed in terms of exponentials, the error function $(\int_0^x e^{-\sigma^2} d\sigma)$, and Dawson's integral $(e^{-x^2}\int_0^x e^{\sigma^2} d\sigma)$. See (a) C. F. Melius, Ph. D. thesis (California Institute of Technology, 1972) (unpublished); (b) C. F. Melius and W. A. Goddard III (unpublished).

[30] We thank Dr. W. J. Hunt for helpful suggestions regarding the matrix-fitting approach for the potential.

[31] The $-Z(\infty)/r = -1/r$ term has been removed before fitting the matrix elements.

[32] The constant A obtained from the fit is not necessarily equal to Z_{NUC}. However, one can constrain A to be equal to Z_{NUC} during the fit.