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Valence Quantum Monte Carlo with *ab initio* effective core potentials*

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I. Introduction

In the electronic structure of molecular systems, one can often make a fairly natural division into core and valence electrons. The valence electrons largely determine chemical properties such as bond strengths, polarizabilities, electron affinities, ionization potentials, as well as molecular geometry. Hellmann [1] and Gombas [2] were the first to replace the core electrons by an effective potential which contains the core-valence repulsion and orthogonality condition. Since then, the efforts of Phillips and Kleinman [3], Goddard and Melius [4], Kahn, Baybutt and Truhlar [5], and Christiansen, Lee and Pitzer [6], have led to the development of *ab initio* effective core potentials (ECP) which have been extensively tested and used over the past several years in conventional, as contrasted to quantum Monte Carlo (QMC), electronic structure studies [7]. Because of its successful inclusion in these approaches, the ECP method is a natural starting point in the investigation of QMC valence-only approaches.

In QMC, the need for a valence-only approach is perhaps even greater than in conventional *ab initio* methods, because the innermost electrons are

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responsible for a sharp increase in the computation time required for heavy-atom systems. Consider a neutral atom of nuclear charge Z. Asymptotically, the CPU time required to compute the energy is determined by the evaluation of the Slater determinant and the two-body potential. For N electrons, these terms are of order N^2. Thus, if the energy is sampled M times during a simulation, the CPU time, T, scales as

$$T \sim M \; Z^2 \, . \tag{1}$$

M is determined by the statistical uncertainty, ϵ, required to resolve the energy of interest, E -- specifically, it is proportional to $(\epsilon/E)^2$. Additionally, for typical (small) time steps, τ, M is inversely proportional to τ. Combining these factors one obtains

$$M \sim \frac{E^2}{\tau \, \epsilon^2}. \tag{2}$$

For energies of chemical interest (*e.g.* binding energies, ionization potentials, *etc.*), ϵ is essentially constant, while the total energy scales roughly as $E \sim Z^2$. In addition, the radius of the inner electrons decreases as Z^{-1} [the hydrogenic wavefunction, $\exp(-Zr)$, contracts by this factor]. Thus τ must decrease to keep step sizes small enough to avoid crossing nodes. Since the distance traveled in one time step is $\Delta R \sim \tau^{1/2}$, then $\tau \sim \Delta R^2 \sim Z^{-2}$. Combining Eqs. (1) and (2), with these substitutions, leads to

$$T \sim Z^8. \tag{3}$$

A somewhat different argument has been given by Ceperley, and yields $Z^{5.5}$ [10].

A very different picture emerges when treating only the valence electrons. Moving across a row of the periodic table, the effective nuclear charge given by, $Z^{eff} = Z - N_{core}$, increases, where N_{core} is the number of core electrons. Thus by the arguement above, E increases and τ decreases. On the other hand, moving

down a column of the periodic table, with Z^{eff} held constant, the valence electrons become more diffuse. In this case E decreases, and τ may be increased. A fit to the SCF valence energies of the second row elements from Ref. [8] yields $E \sim (Z^{eff})^{0.7}$, compared to the previous Z^2 dependence. From the arguments following Eq. (2), τ is expected to scale as E, leading to

$$T \sim (Z^{eff})^{4.1}. \tag{4}$$

This is a significantly lower power than Z^8, and, in addition, Z^{eff} is considerably smaller than Z.

Another difficulty at large Z in all-electron calculations stems from the fixed-node approximation. Although the fixed-node error is typically a very small percentage of the total energy (0.02% for CH_2 [11]), when the total energy is large, the fixed-node error can be a significant fraction of the bond energy. This was found for N_2 [12]. Thus the placement of the inner nodes can dominate the accuracy of the calculation. Treating only the valence electrons leads to a smaller calculated energy and eliminates the core nodes. This should reduce the fixed-node error to well below the bond energy.

In this paper we present an approach for implementing ECP's in QMC, and present results for some atomic and molecular systems. In Sec. II we outline the theory of fixed-node diffusion QMC, the theory of effective core potentials, and the necessary modifications to bring the two together (ECP-QMC). Some results for one- and two-electron systems using the ECP-QMC method are presented in Sec. III. The final section contains concluding remarks on valence-only approaches and the ECP-QMC method used here.

II. Theory

QMC

The fixed-node diffusion QMC approach used in this study has been described in detail in Ref. [9]. Only those points pertinent to ECP's will be reviewed here. As a first step, the time-dependent electronic Schrödinger equation is transformed into

$$\partial f/\partial t = D\nabla^2 f - D\nabla\cdot(\mathbf{F}_Q f) + (E_T - E_L)f \quad . \tag{5}$$

Here

$$f(\mathbf{R},t) \equiv \Psi_I(\mathbf{R})\Psi(\mathbf{R},t), \tag{6a}$$

$$E_L(\mathbf{R}) \equiv \mathbf{H}\Psi_I(\mathbf{R})/\Psi_I(\mathbf{R}), \tag{6b}$$

$$F_Q(\mathbf{R}) \equiv 2\nabla\Psi_I(\mathbf{R})/\Psi_I(\mathbf{R}), \tag{6c}$$

and, D is the "diffusion" constant, $\hbar^2/2m_e$. The importance function, Ψ_I is a compact "guess" at the solution, and is used to improve the efficiency of the technique [9]. $\Psi(\mathbf{R},t)$ is the sought solution. Note that t is an imaginary time, so that at large t, the function $\Psi(\mathbf{R},t)$, decays to Φ_0, the exact lowest-energy eigenstate of the Hamiltonian. Because electrons are Fermions, Φ_0 must be antisymmetric with respect to exchange of electrons. However, the lowest energy eigenstate of the Hamiltonian is symmetric -- *i.e.* a Bose state. The fixed-node approximation [9] forces the Monte Carlo solution to be antisymmetric by imposing the nodes of the importance function Ψ_I onto $\Psi(\mathbf{R},t)$. This corresponds to solving the Schrödinger equation exactly subject to the constraint, $\Phi_0 = 0$ when $\Psi_I = 0$. When Ψ_I is chosen to describe the Fermi ground state, the fixed-node energy can be shown to be a variational bound to the true ground-state energy [9]. Excited states can be obtained through the fixed-node approximation by choosing Ψ_I with the proper nodes [13], but the energy is variational with respect to the true excited state energy only in certain cases.

Equation (5) is simulated by a random walk of an ensemble of $3N$ dimensional points (or "walkers"). Each walker is allowed to drift and diffuse in such a way as to simulate Eq. (5), over a time interval τ. To move the walkers correctly one must use the exact Green's function of the system. This Green's function, however, is not known analytically. Nevertheless, one may sample from it [14], or, in the diffusion QMC approach, use an approximate Green's function that becomes exact as τ approaches zero. This time step bias is then eliminated by extrapolation to zero from several runs performed at different time steps [9].

ECP

The theory of ECP's is now well established in conventional *ab initio* approaches [5], and has been reviewed by Krauss and Stevens [15]. Here we follow the approach of Kahn, *et. al.* [5], and specialize to QMC. The first step is to write a valence-electron Schrödinger equation,

$$\Psi = \Psi_{core} \; \Psi_{val} \tag{7a}$$

$$\mathbf{H}_{val} \, \Psi_{val} = E_{val} \, \Psi_{val} \; , \tag{7b}$$

with,

$$\mathbf{H}_{val} = \sum_{i=1}^{N_{val}} \left(-\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A^{eff}}{r_{iA}} + \sum_{j<i}^{N_{val}} \frac{1}{r_{ij}} \right) + \sum_A \sum_{B<A} \frac{Z_A^{eff} Z_B^{eff}}{R_{AB}} + \mathbf{U}^{ECP} \; .$$

The indices i and j refer to valence electrons, while A and B refer to nuclei. Z^{eff} is the screened nuclear charge seen by the valence electron, and is taken to be $Z - N_{core}$. The core-valence repulsion and the core-valence orthogonality condition are replaced by the *non-local* pseudopotential [5],

$$\mathbf{U}^{ECP} = \tag{8}$$

$$\sum_A \sum_{i=1}^{N_{val}} \left(U_{l_{\max}+1}^A (r_{iA}) + \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} \mid Y_{lm}(\Omega_{iA}) > U_l^A(r_{iA}) < Y_{lm}(\Omega_{iA}) \mid \right) ,$$

where the sum on A is over only those centers having a pseudopotential. For

center A , Ω_{iA} is the solid angle of electron i from A , $l_{\max}$ is the largest orbital angular momentum among the core electrons, U_l^A is a radial pseudopotential for atom A which depends only on the electron-nuclear distance, r_{iA} , and the angular momentum, l . The spherical harmonics, Y_{lm} , act as projection operators, insuring the correct orthogonality between the missing core and the valence wavefunction [16]. The functions U_l^A are generally obtained in numerical form from atomic Hartree-Fock calculations. Typically they are then fit to functions of the form,

$$U_l(r) = \frac{1}{r^2}\sum_k d_{kl}\, r^{n_{kl}}\, e^{-b_{kl} r^2} , \tag{9}$$

with n_{kl} taking on values of 0, 1, and 2.

ECP-QMC

For QMC the non-local ECP operator must be rendered in a local form. This is simply accomplished by allowing $\mathbf{U}^{ECP}$ to act on Ψ_{val} as implied in Eq. (6b). This leads to an additional term in the local energy, namely

$$U_{Local}^{ECP} = \tag{10}$$

$$\sum_A \sum_{i=1}^{N_{val}} \left[U_{l_{\max}+1}^A(r_{iA}) + \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} Y_{lm}(\Omega_{iA})\, U_l^A(r_{iA}) < Y_{lm}(\Omega_{iA}) \mid \Psi_{val} > / \Psi_{val} \right],$$

where Ψ_{val} becomes the QMC valence importance function.

Although the theory can be applied to multi-determinant functions, it is sufficient for present purposes to consider a single determinant function,

$$\Psi_{val} = \det \mid \phi_1(1) \cdots \phi_i(i) \cdots \phi_n(n) \mid ,$$

where the ϕ_i are molecular orbitals. Since the local ECP, Eq. (10), is a sum over one-electron operators, one need consider only a single column at a time of the Slater matrix. Thus, by expanding the determinant in co-factors of electron i , the angular integral may be written

$$< Y_{lm}(\Omega_{iA}) \mid \Psi_{val} > / \Psi_{val} = \sum_j D_{ji}^{-1} < Y_{lm}(\Omega_{iA}) \mid \phi_j(i) > , \tag{11}$$

where we have used the property that the elements of the inverse of the Slater matrix, D_{ji}^{-1}, are the transpose of the co-factors divided by the determinant. Next, expanding the molecular orbitals in single-particle basis functions, χ, we obtain

$$< Y_{lm}(\Omega_{iA}) \mid \phi_j(i) > = \sum_{p=1}^{N_{basis}} c_{jp} \int d\Omega_{iA}\, Y_{lm}(\Omega_{iA}) \chi_p(\mathbf{r}_i) . \tag{12}$$

The basis functions, χ, are taken to be Cartesian Gaussian-type functions (GTF's), which have the general form

$$\chi = N_{uvw}(\varsigma)\, x^u\, y^v\, z^w \exp(-\varsigma r^2) , \tag{13}$$

where $N_{uvw}(\varsigma)$ is the standard normalization factor [19]. In (12), the sum over basis functions can be usefully broken up into functions centered on atom A (with the ECP) and functions centered on all remaining atoms. Thus the right hand side of Eq. (12) becomes

$$\sum_{p=1}^{N_{basis}^A} c_{jp} \int d\Omega_{iA}\, Y_{lm}(\Omega_{iA}) \chi_p(\mathbf{r}_{iA}) + \sum_{B \neq A} \sum_{p=1}^{N_{basis}^B} c_{jp} \int d\Omega_{iA}\, Y_{lm}(\Omega_{iA}) \chi_p(\mathbf{r}_{iB}) \tag{14}$$

where N_{basis}^A and N_{basis}^B are the number of basis functions centered on atoms A and B, respectively.

To evaluate the integral involving only atomic center A, note that

$$\sum_{m=-l}^{l} Y_{lm}(\Omega_{iA}) \int d\Omega_{iA}\, Y_{lm}(\Omega_{iA}) \chi_p(\mathbf{r}_{iA}) = \delta_{l,l_p}\, \chi_p(\mathbf{r}_{iA}) \tag{15}$$

where l_p is the electronic orbital-angular-momentum quantum number of basis function p. Thus, combining Eqs. (10) - (12), and (14), performing the sum over m and l, and using (15), the single-center term for electron i in molecular orbital j is

$$u_{ij}^{AA} \equiv D_{ji}^{-1} \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} Y_{lm}(\Omega_{iA}) U_l^A(r_{iA}) \sum_{p=1}^{N_{basis}^A} c_{jp} \int d\Omega_{iA}\, Y_{lm}(\Omega_{iA}) \chi_p(\mathbf{r}_{iA}) \tag{16}$$

$$= D_{ji}^{-1} \sum_{p=1}^{N_{basis}^A} c_{jp}\, \chi_p(\mathbf{r}_{iA}) U_{l_p}^A(r_{iA}) .$$

For the integrals involving two centers, basis functions on center B must be expanded around center A. To this end Kahn, *et. al.* [5] have shown that

$$x_{iB}^u y_{iB}^v z_{iB}^w e^{-\varsigma r_{iB}^2} = e^{-\varsigma r_{iA}^2} \Bigg\{ e^{-\varsigma R_{AB}^2} \sum_{r=0}^{u} \sum_{s=0}^{v} \sum_{t=0}^{w} \binom{u}{r} \binom{v}{s} \binom{w}{t} X_{AB}^{u-r} Y_{AB}^{v-s} Z_{AB}^{w-t}\, r_{iA}^{r+s+t}$$

$$\times\, 4\pi \sum_{\lambda=0}^{\infty} M_\lambda(2\varsigma R_{AB}\, r_{iA}) \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}(\Omega_{AB})\, \hat{x}_{iA}^r\, \hat{y}_{iA}^s\, \hat{z}_{iA}^t\, Y_{\lambda\mu}(\Omega_{iA}) \Bigg\} \tag{17}$$

where $\hat{x} \equiv x/r$ (the angular part of the Cartesian coordinate x), and M_λ is a modified spherical Bessel function of the first kind [20]. Substituting (17) into the second term of (14), and temporarily ignoring all the radial terms, the angular integral is of the form

$$\int d\Omega\, Y_{lm}(\Omega)\, \hat{x}^r\, \hat{y}^s\, \hat{z}^t\, Y_{\lambda\mu}(\Omega) \equiv \Omega_{\lambda\mu lm}^{rst} . \tag{18}$$

The Y_{lm} may be expressed in terms of $\hat{x}$, $\hat{y}$, and $\hat{z}$,

$$Y_{lm} = \sum_{a=0} \sum_{b=0} \sum_{c=0}^{a+b+c=l} g_{abc}^{lm}\, \hat{x}^a\, \hat{y}^b\, \hat{z}^c , \tag{19}$$

which leads to

$$\Omega_{\lambda\mu lm}^{rst} = \sum_{a,b,c}^{a+b+c=l} \sum_{d,e,f}^{d+e+f=\lambda} g_{abc}^{lm}\, g_{def}^{\lambda\mu}\, I(r+a+d, s+b+e, t+c+f) .$$

The elementary integral $I(i,j,k)$ [17] is

$$I(i,j,k) \equiv \int d\Omega\, \hat{x}^i\, \hat{y}^j\, \hat{z}^k = \begin{cases} \dfrac{(i-1)!!(j-1)!!(k-1)!!}{(i+j+k+1)!!} & \text{i,j,k all even} \\ 0 & \text{otherwise .} \end{cases} \tag{20}$$

Note that the elements of $\Omega^{rst}_{\lambda\mu lm}$ are constants, and so may be calculated once and tabulated.

Thus, the two-center term for electron i in molecular orbital j [combining Eqs. (10) - (14) with (17) and (18)] is

$$u^{AB}_{ij} = D^{-1}_{ji} \sum_{p=1}^{N^B_{basis}} c_{jp}\, N_{u_p\, v_p\, w_p}(\varsigma_p)\, e^{-\varsigma_p r^2_{iA}}$$

$$\times \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \sqrt{4\pi}\, Y_{lm}(\Omega_{iA})\, U^A_l(r_{iA})\, \mathbf{F}^p_{lm}(r_{iA}, \mathbf{R}_{AB}). \tag{21}$$

All the complicated behavior of Eq. (17) has been lumped into the single term, $\mathbf{F}^p_{lm}$, which is,

$$\mathbf{F}^p_{lm}(r,\mathbf{R}) \equiv e^{-\varsigma_p R^2} \sum_u^{u_p} \sum_v^{v_p} \sum_w^{w_p} \begin{pmatrix} u_p \\ u \end{pmatrix} \begin{pmatrix} v_p \\ v \end{pmatrix} \begin{pmatrix} w_p \\ w \end{pmatrix} X^{u_p - u}\, Y^{v_p - v}\, Z^{w_p - w}\, r^{u+v+w}$$

$$\times \sum_{\lambda=0}^{u_p+v_p+w_p+l} M_\lambda(2\varsigma_p R r) \sum_{\mu=-\lambda}^{\lambda} \sqrt{4\pi}\, Y_{\lambda\mu}(\Omega)\, \Omega^{uvw}_{\lambda\mu lm}\ , \tag{22}$$

where X, Y, Z, R, and Ω, are the Cartesian and polar coordinates of $\mathbf{R}$, the internuclear vector, and r is the distance from the ECP atom (A) to the electron.

Returning to the original expression for the local ECP, Eq. (10) can now be written in terms of u^{AA}_{ij} and u^{AB}_{ij},

$$U^{ECP}_{Local} = \sum_A \sum_{i=1}^{N_{val}} \left(U^A_{l_{max}+1}(r_{iA}) + \sum_j \left[u^{AA}_{ij} + \sum_{B \neq A} u^{AB}_{ij} \right] \right). \tag{23}$$

For an atom, only the u^{AA}_{ij} term is needed, and the expressions are greatly simplified. In the molecular case, the evaluation of u^{AB}_{ij} takes roughly 15 times

longer to compute than the rest of E_{local}. One method for reducing the time required is to fit numerically the r dependence of u_{ij}^{AB} [Eq. (21)] prior to the QMC run. This may be done either by interpolation on a grid, or by splines, or with a suitable expansion, such as

$$\sum_p c_{jp} N_p e^{-\zeta_p r^2} U_l^A(r) \mathbf{F}_{lm}^p(r_{ia}, \mathbf{R}_{AB}) = \sum_\nu C_\nu r^{N_\nu} e^{-\zeta_\nu r^2} . \tag{24}$$

This procedure would have to be carried out for each choice of importance function and geometry.

Slater-type functions and correlation functions

Thus far in this development, GTF's have been used because the resulting integrals, Eq. (14), are relatively simple. Additionally, GTF's are standard in conventional *ab initio* molecular-orbital approaches because electronic integrals take on a particularly simple analytic form [21,22]. In all-electron QMC, however, no analytic integration is necessary. Instead, a smooth local energy surface $[E_L(\mathbf{R})]$ is required to reduce the variance of the random walk, and thus the computation time needed to achieve the desired statistical uncertainty. Importance functions constructed from GTF's do not result in the necessary smooth $E_L(\mathbf{R})$ surface. Thus it has been common in QMC to use Slater-type functions (STF's) in a Slater determinant, and to multiply the determinant by an electron-electron correlation function (EECF) and an electron-nuclear correlation function (ENCF). Frequently Pade-Jastrow forms are used for the pair correlation factors [9]. This form for Ψ_I not only gives a smoother E_L surface, but also satisfies the electron-nuclear and electron-electron cusp conditions [9]. Since the GTF importance functions described for the ECP-QMC approach have incorrect short and long range behavior, and cannot satisfy either cusp condition, it is expected that these simulations will be less efficient than those with an STF + EECF + ENCF importance function.

In ECP-QMC, however, analytic integration of the importance function becomes necessary, and GTF's are the simplest basis functions to integrate. In principle STF's and correlation functions can also be included analytically, though at an additional computational cost. However, in one special case STF's can be used readily. As noted in Sect. II, for atoms only the u_{ij}^{AA} term [Eq. (16)] needs to be evaluated. Furthermore, Eq. (16) applies to any basis function centered on the ECP atom, as long as it has a definite orbital angular momentum, l. Thus STF's and ENCF's can be used directly for an atom, or for an ECP atom in a molecule involving a single ECP center (the other centers would require a GTF basis).

For the general case, when STF's are included in the basis set there are several options for evaluating the two-center term of Eq. (14). One option is to analytically expand all STF's about the ECP center, as was done for the GTF's in Eq. (17) [23]. Unfortunately, this expansion is much more cumbersome than Eq. (17). Another approach for including STF's involves numerical integral evaluation. Possibly the best option is to expand the STF's in terms of GTF's and to proceed as in Eq. (17). This could be done either by a least squares fit, as in the STO-nG basis sets [24], or by a Gaussian integral transform [25]. Of these alternatives, the least squares method is the simplest, and in fact one can simply replace the STF basis set by the equivalent STO-nG basis set in the importance function itself. This would mimic the correct shape of the STF's. Furthermore, if an ENCF were included, the electron-nuclear cusp condition could also be satisfied.

Correlation functions can be treated in a manner similar to the STF's. In particular, a suitable expansion or numerical technique can be employed. One advantage here is that both the ENCF and EECF are constant away from the region where the pair of particles meet. The ENCF is effectively constant unless

an electron is inside a core. An electron should not be found frequently inside an ECP core due to the strong repulsion within the ECP. An electron inside a *different* core will result in a contribution to the ENCF, but U_l^A is small there. Thus there is effectively no contribution to U_{Local}^{ECP} in either case. A similar result is found for the EECF. The only EECF contribution to the energy occurs when two electrons are close together, and both electrons must be in the core region of a nucleus with an ECP for a contribution to U_{Local}^{ECP} [*c.f.* Eq. (16)]. Thus, to a good approximation, the EECF's may be factored out of the angular integral as well. Factoring out the correlation functions can be viewed either as an approximation to the integral, or as a modification of the pseudopotential. In either case, the effect on the energy must be examined to insure that the results are not biased by this treatment.

III. Results

The above-described ECP-QMC approach has been implemented and tested on a number of atomic and molecular systems. The compact effective potentials (CEP) of Stevens, Basch, and Krauss [8] were used in all the calculations presented here because they are computationally faster than other published sets of ECP's [26]. The basis set used in all calculations consists of only the four Gaussian functions given with the CEP. Except where noted, no correlation functions have been used. In the systems studied only one- and two-valence electrons are present, so there is no fixed-node approximation. Thus we can fairly assess the quality of the ECP approximation, as this is the only approximation present (QMC solves Eq. (7b) exactly).

Table 1 presents ECP-QMC results for the electron affinities of Li and Na, as well as the ionization potential of Mg. For comparison, HF and CI results are

also given as well as experimental values. ECP-QMC is comparable in quality to the CI results, and also in all cases contains the experimental result within its error bars (~ 0.02 eV). Thus, the approximation made in replacing the core electrons by a pseudopotential appears to be accurate within the given error bars for these data.

The Na_2 molecule is an good example of a system presently out of the range of an all-electron QMC calculation. With a total energy of about -320 hartree [31], and an experimental binding energy of only 0.0275 hartree [39], a statistical uncertainty of less than 5-10 parts per million would be required in a QMC run with 22 electrons. Furthermore, the potential energy curve is very flat, and resolution of energies at bond lengths 0.8 bohr apart would further require a statistical uncertainty of less than 2 parts per million. However, for ECP-QMC the valence energy is only 0.3925 hartree, meaning that our present statistical uncertainty of 0.2% is sufficient to resolve the binding energy and points on the potential energy curve.

Table 2 gives a comparison of binding energies for Na_2 and Fig. 1 shows computed and experimental potential-energy curves. The ECP-QMC energies are again comparable to available all-electron MCSCF results, and agree with experiment to within statistical uncertainty. Note in Fig. 1 that even though the MCSCF minimum is within the statistical uncertainty of the ECP-QMC energy, it is displaced toward longer bond length, while the ECP-QMC points are consistent with the experimental curves in all cases.

Finally, the binding energy for NaH is given in Table 3, along with other theoretical results and the experimental values. The previously discussed systems (Li, Na, Mg, and Na_2) had ECP's on all centers. In these cases the GTF basis set performed well. However, for NaH, the H atom has no ECP. A standard 4-GTF

basis set for the H atom results in such a large variance that it is not usable. Instead we have used a double-zeta STO-6G basis set with an ENCF on the H atom (*c.f.* Sec. II). The effect of the ENCF on the energy was tested by performing calculations both with and without it present. The computed energy is the same in both cases, but the variance decreased with the ENCF. Note that neither the double-zeta STO-6G basis set, nor the ENCF alone is sufficient to reduce the variance to an acceptable level. This suggests that both the shape and the cusp of the STF are necessary for describing the region near the H nucleus. In addition, we found that exponents for an STO-6G basis optimized with respect to its SCF dipole moment (6.3 D, vs. experiment, 6.4 D [40]), resulted in a significantly lower variance in the fixed-node energy than exponents optimized with respect to the SCF energy (which produced an SCF dipole moment of 7.3 D). This presumably is due to the more accurate charge distribution of the dipole-moment-optimized SCF function. Clearly, when treating systems with core electrons with a GTF basis set, great care must be taken in selecting Ψ_I.

IV. Conclusions

In this paper we have shown how ECP's may be incorporated into QMC. Using the ECP-QMC approach, we have calculated the exact energies (within the given statistical uncertainty) for the CEP's of Stevens, Krauss, and Basch, for some one- and two-valence electron systems. These energies are found to give excellent agreement with experiment for electron affinities, ionization potentials, and bond strengths.

It should be noted, however, that ECP's are not the only valence-only avenue open to QMC. In addition to adapting other conventional approaches (model potentials, pseudopotentials from density-functional methods, *etc.*), there are

some uniquely QMC methods that hold promise. Moskowitz [45] has suggested replacing the electron-electron potential due to the core electrons with the Hartree-Fock mean-field potential, and using a Hartree-Fock importance function to reduce the variance due to the core energy. Another approach, which we are currently developing, is a method for treating the core and valence electrons on different time scales in the simulation, effectively "freezing" the core during a valence QMC walk. This is combined with a differential QMC technique to suppress fluctuations due to the core [46]. Each of these methods has advantages and disadvantages as to level of approximation involved and computational speed obtained. The potential inherent in valence-only techniques (in QMC, as well as in conventional approaches), means that all possibilities need to be explored. ECP-QMC as one such approach appears to work well and larger systems of chemical interest need to be explored.

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Figure Captions

Figure 1. Potential energy curves for Na_2.
Solid circles, this work; open circles, all-electron MCSCF, Ref. [33]; dashed line, spline fit to experimental points of Ref. [38]; solid line, spline fit to experimental points of Ref. [39].

Table 1. Electron affinities and ionization potentials of one- and two-valence electron atoms. Energies in eV.

Atom/Ion	HF[a]	CI[b]	QMC-ECP	Experiment
Li/Li^-	-0.122	0.615	0.611(20)	0.620(7)[c]
Na/Na^-	-0.116	0.539	0.555(21)	0.546(5)[c]
Mg/Mg^+	6.613	7.524	7.637(26)	7.646[d]

[a] Ref. [27]
[b] Ref. [28]
[c] Ref. [29]
[d] Ref. [30]

Table 2. Binding energy for Na_2.

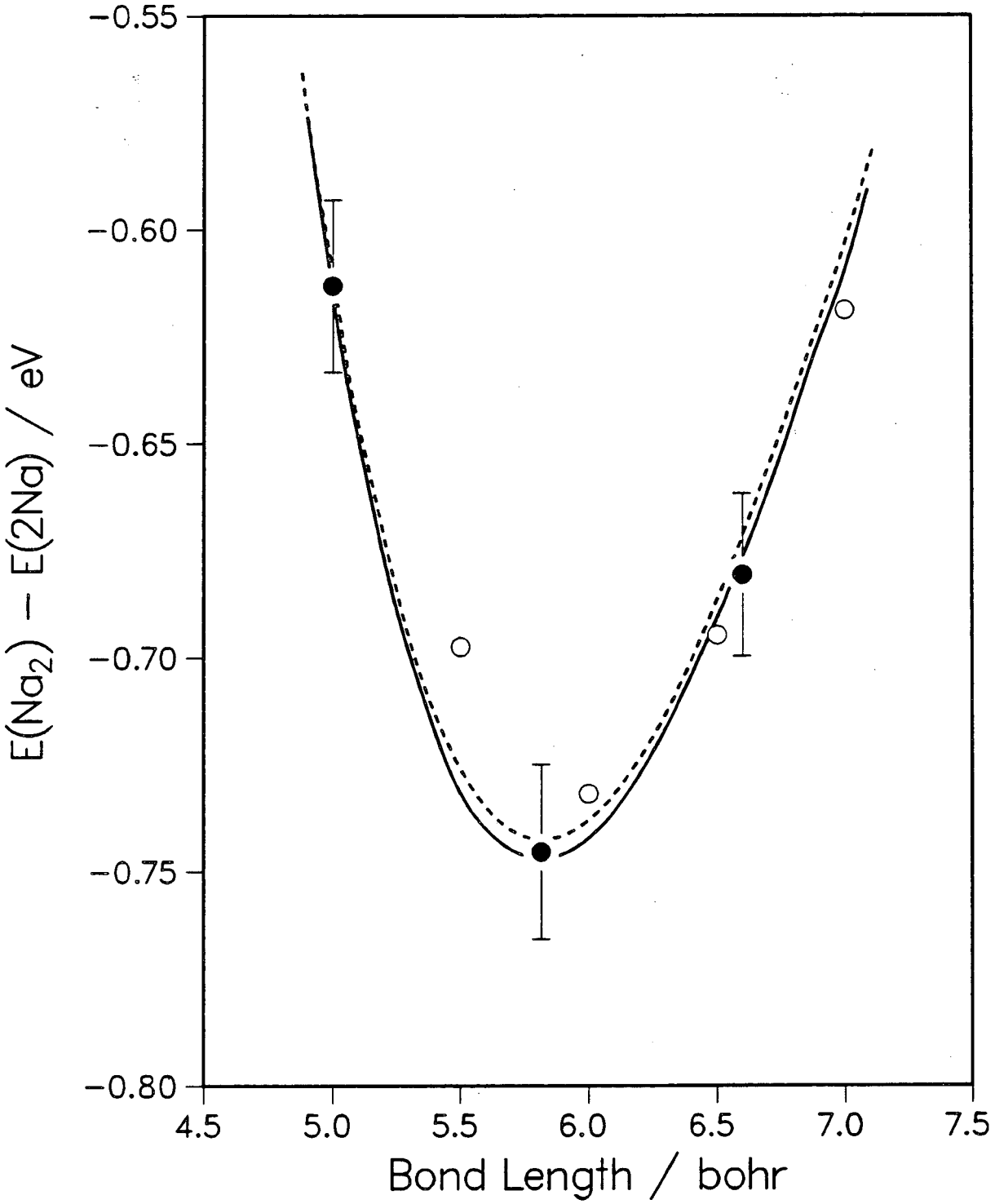
	Method	D_e (eV)
All electron	HF[a]	-0.022
	MCSCF[b]	0.732
	MBPT[c]	0.650
Valence electron	LDFT[d]	0.69
	CI[e]	0.73
	CVCI[f]	0.747
	ECP-QMC[g]	0.746(20)
Experiment	45 vib. spect.[h]	0.7424(25)
	56 vib. spect.[i]	0.7469(7)

[a] Near Hartree-Fock limit, Ref. [32].
[b] Multi-configuration SCF, Ref. [33].
[c] Quasi-degenerate many-body perturbation theory, Ref. [34].
[d] Local spin-density functional, Ref. [35].
[e] Configuration interaction, Ref. [36].
[f] CI with a perturbation theory estimate of the core-valance interaction, Ref. [37].
[g] This work.
[h] RKR analysis of vibrational spectrum using levels through v''=45, Ref. [38].
[i] Same as h, except using levels through v''=56, Ref. [39].

Table 3. Binding energy for NaH

	Method	D_e (eV)
All electron	HF[a]	0.932
	CI[b]	1.922
	CEPA[c]	1.920
Valence electron	MCSCF[d]	1.885
	ECP-QMC[e]	1.954(73)
Experiment	11 vib. spect.[f]	1.9714

[a] Near Hartree-Fock limit, Ref. [41]
[b] Configuration interaction, Ref. [42].
[c] Coupled-electron pair approximation, Ref. [43].
[d] Model potential multi-configuration SCF, Ref. [44].
[e] This work.
[f] RKR analysis of vibrational spectrum using levels through $v''=11$, Ref. [40].


−0.55
−0.60
−0.65
−0.70
−0.75
−0.80
E(Na2) − E(2Na) / eV
4.5
5.0
5.5
6.0
6.5
7.0
7.5
Bond Length / bohr

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