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Calculating atomic properties using variational Monte Carlo

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Using variational Monte Carlo and the explicitly-correlated wave function forms optimized by Schmidt and Moskowitz, we compute a number of properties for the atoms He–Ne. The expectation value of the Hamiltonian using these wave functions contains between 70.0% and 99.8% of the correlation energy for the neutral atoms (17 parameters), 60.8% and 99.1% for selected cations (9 parameters), and 73.9% and 89.4% for selected anions (17 parameters). For those properties which sample the valence region, our results are in good agreement with previous calculations (where available). Because of a defect in the wave function form, a substantial error is found in those properties which two electrons that are in close proximity. © *1995 American Institute of Physics.*

I. INTRODUCTION

Variational Monte Carlo uses Monte Carlo integration to calculate the expectation value

$$\langle A \rangle = \sum_i \ (\Psi_i A \Psi_i / w_i) \ \bigg/ \sum_i \ (\Psi_i^2 / w_i) \tag{1}$$

and variance

$$\sigma_A^2 = \sum_i \ [(A\Psi_i - \langle A \rangle \Psi_i)^2 \Psi_i^2 / w_i^2] \ \bigg/ \bigg[\sum_i \ (\Psi_i^2/w_i) \bigg]^2 \tag{2}$$

of a trial wave function and an operator.[1–16] Here $\Psi_i = \Psi_t(x_i)$ is the value of the trial wave function at the Monte Carlo integration point x_i and $w_i = w(x_i)$ is the relative probability of choosing this point. Because no analytic integrals need be determined, even complicated operators acting on highly nonlinear wave function forms are usually easy to evaluate.

In this paper we use the largest atomic wave functions of Schmidt and Moskowitz[10,15]

$$\Psi_t = \det^{\text{up}} \det^{\text{down}} \exp\bigg[\sum_{i<j} \sum_{k=0} c_k (q_i^n q_j^l + q_j^n q_i^l) q_{ij}^m \bigg] \tag{3}$$

to compute a number of properties for the first row atoms He–Ne. Here n, l, and m are integers (0,1,...) which have been preselected for each value of k, c_k are the optimized values from Refs. 10 and 15, det is the Hartree–Fock determinant calculated using the Slater orbital functions of Clementi and Roetti,[17] and $q = r/(r+1.0)$. Unless otherwise indicated, all values in this paper are given in atomic units.

II. GENERATING CONFIGURATIONS

As in previous papers we can generate the configurations, x_i, and weights, $w(x_i)$, "biased as random," i.e., from an importance function which was chosen so as to minimize the variance of the total energy.[14] For systems with only a few electrons this method is relatively straightforward to implement and gives good results. As the number of electrons is increases, however, the percentage of configurations placed in the important regions of the wave function (referred to as N_{eff} in previous papers) quickly drops. Such a situation is shown in Table I. One could compensate for this

decrease by simply using a larger number of configurations but it is more efficient to instead modify the way in which each configuration is generated.

The main reason that the biased-as-random method deteriorates as more electrons are added is because it includes no information about the nodes in the wave function. In these regions of space, the wave function is not important and so generating large numbers of configurations there is inefficient. One way to include some nodal information in the configurations is by choosing them from a "single average." This procedure consists of the following steps:

(1) Generate a small number, M, of coordinates, x_i^{up}, and weights, $w(x_i^{\text{up}})$, for each spin up electron using the biased-as-random method.

(2) For each of these configurations calculate the Hartree–Fock spin-up determinant, $\Phi(x_i^{\text{up}})$.

(3) Generate a random number, R, such that $0 < R < \sum_{i=1}^{M}[\Phi(x_i^{\text{up}})^2/w(x_i^{\text{up}})]$.

(4) Select a single configuration from the original set of M by finding the one at which $\sum_{i=1}^{j}[\Phi(x_i^{\text{up}})^2/w(x_i^{\text{up}})]$ first becomes larger than R. The probability of generating x_j^{up} is given by

$$w(x_j^{\text{up}}) = \frac{\Phi(x_j^{\text{up}})^2}{\dfrac{1}{M} \displaystyle\sum_{i=1}^{M} \dfrac{\Phi(x_i^{\text{up}})^2}{w(x_i^{\text{up}})}}.$$

(5) Repeat steps 1–4 for the spin down electrons.

The full single-averaged configuration thus requires $M x_j^{\text{up}}$ evaluations plus $M x_j^{\text{down}}$ evaluations to determine both it and its weight $w(x_j^{\text{up}}) w(x_j^{\text{down}})$. Since they contribute little to the sum, those configurations which are generated near nodes will be de-emphasized by this procedure. The probability of finding an important configuration is changed from approximately M^{-2} to 1.0. The price paid for this is the generation of M extra configurations for every one selected. As Table I shows, the statistical error for $M=10$ rises relatively slowly as a function of the number of electrons (except for beryllium because a single determinant cannot remove the $2s-2p$ degeneracy in this system). In fact, the ratio of the variance and the total energy remains almost constant. This suggests that this method could easily be extended to larger systems.

TABLE I. A comparison of atomic energies and their variances using 4000 Monte Carlo integration points generated by two methods. The value in parentheses is N_{eff}.

System	Method 1[a]		Method 2[b]	
He	−2.903 22±0.000 46	(2882)	−2.903 22±0.000 46	(2882)
Li	−7.476 7 ±0.001 9	(717)	−7.478 6 ±0.001 7	(3022)
Be	−14.641 ±0.088	(526)	−14.637 ±0.038	(2785)
B	−24.629 ±0.018	(218)	−24.612 2 ±0.007 6	(2004)
C	−37.848 ±0.036	(117)	−37.806 ±0.013	(1393)
N	−54.472 ±0.068	(127)	−54.574 ±0.020	(1609)
O	−75.053 ±0.078	(89)	−75.048 ±0.023	(1216)
F	−99.781 ±0.091	(71)	−99.643 ±0.028	(1169)
Ne	−128.81 ±0.13	(53)	−128.890 ±0.035	(1072)

[a]Guiding function optimization only.
[b]Guiding function optimization+single averaging ($M=10$) to include nodal information.

III. CALCULATING ATOMIC PROPERTIES

For each system we optimized separate guiding functions using 4000 biased-as-random configurations. Previous studies have shown that the guiding function which minimizes the statistical error in the total energy is also good for most other properties (e.g., r_{12}^2) because they depend heavily on those regions where the error in the trial wave function is large.[14] Some properties (e.g., p^4), however, have such a radically different functional form that one can obtain a large decrease in the variance by optimizing a separate guiding function for each of them.[14] For reasons which will shortly become evident, we have computed all quantities using only the guiding function which minimizes the statistical error in the total energy.

In Table II we present our results. These properties were computed using 1 024 000 single-averaged configurations. Because of cancellations between the potential and kinetic energies, the total energy has a much lower variance than other expectation values. Despite this, we are generally able to determine many properties to two or three significant figures. Most of our values are in good agreement with the more traditional calculations shown in Table III although many of these quantities have not been previously computed or have been only calculated with Hartree–Fock wave functions. A noticeable exception is p_i^4. Although our values agree with earlier results for those systems which have only s-type orbitals, they differ with them for those systems which also contain p-type orbitals. As the number of p-type orbitals grow, this difference becomes significant. For neon our result, 1439(20), is hundreds of standard deviations away from both an accurate CI value, 98 719.06,[30] and the SCF value, 99 061.[29] This discrepancy is not an artifact of the Monte Carlo. If we remove the correlation factor from Eq. (3), we obtain the same SCF result as Ref. 29. The most likely reason for this problem is the lack of orbital and spin dependence in the correlating factor. The property p_i^4 contains both r_i^{-2} and r_{ij}^{-2}. The former has a dramatic effect

TABLE II. Selected properties (in a.u.) of various atomic systems generated using variational Monte Carlo with 1024000 single-averaged configurations. The value in parentheses is the variance. The wave functions are those of Schmidt and Moskowitz.

Property	He (^1S)	Li$^+$ (^1S)	Li (^2S)	Be$^+$ (^2S)	Be (^1S)	B (^2P)	B$^-$ (^3P)	C$^+$ (^2P)	C (^3P)	C$^-$ (^4S)
E	−2.903 63(3)	−7.279 5(1)	−7.476 6(2)	−14.318 9(4)	−14.639(2)	−24.617 4(5)	−24.626 3(8)	−37.385 0(9)	−37.805(1)	−37.852(1)
% Corr.	99.8	99.1	96.7	87.7	70.0	70.7	73.9	66.9	74.4	78.4
p_i^2	5.814(7)	14.56(2)	14.93(2)	28.58(4)	29.20(4)	49.19(8)	49.4(2)	74.6(1)	75.5(2)	75.8(2)
r_i	1.856(2)	1.145(1)	5.163(5)	3.183(3)	6.315(5)	6.864(6)	11.56(1)	4.988(4)	7.198(6)	10.550(9)
r_i^{-1}	3.381(3)	5.378(5)	5.700(6)	7.955(8)	8.387(8)	11.39(1)	11.63(1)	14.14(2)	14.70(2)	15.03(2)
r_i^2	2.377(3)	0.892(1)	20.10(3)	6.91(1)	18.80(2)	16.18(2)	43.66(9)	8.159(9)	14.02(2)	27.5(4)
r_i^{-2}	12.06(2)	29.90(3)	29.7(3)	56.9(8)	56.9(5)	97(3)	108(13)	144(8)	142(3)	139(2)
p_i^4	108.3(2)	595(1)	612(10)	2 000(16)	2 111(26)	5 185(67)	5 299(77)	8 450(55)	8 338(70)	9 151(139)
r_{ij}	1.419(2)	0.861(1)	9.010(7)	5.426(4)	15.84(1)	22.61(1)	48.06(3)	16.239(8)	29.19(1)	51.49(2)
r_{ij}^{-1}	0.948(1)	1.570(2)	2.176(2)	3.216(3)	4.319(4)	7.653(6)	8.867(7)	10.085(7)	12.493(9)	14.448(9)
r_{ij}^2	2.506(3)	0.926(1)	40.34(5)	13.87(1)	57.78(5)	68.45(5)	227.8(2)	34.46(2)	74.29(5)	173.1(1)
r_{ij}^{-2}	1.46(1)	4.05(3)	4.33(4)	8.9(1)	9.51(8)	17.3(1)	17.8(2)	27.4(2)	29.5(3)	30.2(3)
$\nabla_i * \nabla_j$	−0.157(2)	−0.279(5)	−0.295(5)	−0.419(9)	−0.46(1)	−0.28(2)	−0.21(2)	−0.19(3)	0.37(4)	0.49(4)
$\langle \delta(r_i) \rangle$	3.624(4)	13.72(2)	13.84(1)	35.14(3)	35.47(3)	72.20(7)	71.99(8)	128.9(1)	128.0(2)	127.8(1)

Property	N$^+$ (^3P)	N (^4S)	O$^+$ (^4S)	O (^3P)	O$^-$ (^2P)	F$^+$ (^3P)	F (^2P)	F$^-$ (^1S)	Ne$^+$ (^2P)	Ne (^1S)
E	−54.011(1)	−54.552(3)	−74.527(2)	−75.018(2)	−75.070(4)	−99.035(2)	−99.689(3)	−99.814(4)	−128.095(3)	−128.895(3)
% Corr.	73.7	80.1	79.5	80.9	84.6	78.6	86.9	89.4	85.4	89.2
p_i^2	108.5(5)	109.2(2)	149.3(5)	149.8(4)	152(2)	195.9(5)	200.2(7)	200.1(7)	255.9(8)	258(1)
r_i	5.519(4)	7.404(6)	5.851(5)	7.718(7)	10.41(1)	6.185(5)	7.864(6)	10.28(1)	6.441(5)	7.905(6)
r_i^{-1}	17.69(2)	18.35(2)	21.60(3)	22.25(3)	22.67(3)	25.64(3)	26.56(3)	27.05(3)	30.32(3)	31.14(3)
r_i^2	7.99(1)	12.33(1)	7.462(8)	11.64(2)	20.76(4)	7.111(7)	10.69(1)	18.28(5)	6.828(6)	9.47(1)
r_i^{-2}	191(1)	196(5)	260(5)	264(5)	254(3)	326(4)	338(5)	332(5)	426(12)	417(6)
p_i^4	9 421(66)	9 045(74)	6 824(44)	6 733(77)	8 719(72)	3 054(33)	4 327(45)	3 987(40)	1 909(18)	1 439(20)
r_{ij}	22.25(1)	35.60(1)	27.99(1)	42.92(2)	66.53(3)	34.11(1)	49.59(2)	73.55(3)	40.33(1)	55.63(2)
r_{ij}^{-1}	15.83(1)	19.21(1)	23.71(1)	27.87(1)	31.36(2)	33.73(2)	39.27(2)	43.65(2)	46.76(2)	53.44(2)
r_{ij}^2	42.56(3)	78.17(4)	47.59(3)	85.72(5)	172.4(1)	52.63(3)	89.50(5)	170.3(2)	57.46(2)	88.99(4)
r_{ij}^{-2}	43.1(3)	47(2)	64.9(6)	68.3(3)	72(2)	93.4(5)	101(2)	104(1)	134.0(9)	140.7(9)
$\nabla_i * \nabla_j$	1.04(5)	1.73(5)	3.04(8)	3.59(8)	3.79(9)	5.8(1)	7.0(1)	7.0(1)	10.5(1)	10.9(1)
$\langle \delta(r_i) \rangle$	208.5(2)	207.6(2)	315.4(4)	313.0(4)	312.9(4)	448.4(5)	451.6(5)	450.5(6)	624.8(7)	623.8(8)

TABLE III. Properties (in a.u.) comparable to those in Table II from some previously published studies.

Property	Li (^2S)	Be (^1S)	B (^2P)	C (^3P)	N (^4S)	O (^3P)	F (^2P)	Ne (^1S)
E	−7.478 060 3 [18]	−14.667 37(3) [22]	−24.653 91 [24]	−37.844 99 [24]	−54.589 3 [24]	−75.067 3 [24]	−99.733 7 [24]	−128.938 8 [24]
p_i^2	14.955 [19]	29.332 9 [23]	49.058ᵃ [25]	75.376ᵃ [25]	108.80ᵃ [25]	149.62ᵃ [25]	198.82ᵃ [25]	257.751 [26]
r_i	4.989 538 [19]	6.128 78ᵃ [20]	6.810 6ᵃ [20]	7.144 6ᵃ [20]	7.350 0ᵃ [20]	7.698 8ᵃ [20]	7.777 6ᵃ [20]	7.891 1ᵃ [20]
r_i^{-1}	5.718 109 [19]	8.408 8ᵃ [20]	11.379 4ᵃ [20]	14.689 5ᵃ [20]	18.335 9ᵃ [20]	22.259 3ᵃ [20]	26.518 6ᵃ [20]	31.113 3ᵃ [20]
r_i^{-2}	18.354 74 [19]	17.318 2ᵃ [20]	15.851 0ᵃ [20]	13.792 1ᵃ [20]	12.772 2ᵃ [20]	11.168 6ᵃ [20]	10.234 0ᵃ [20]	9.371 8ᵃ [20]
r_i^2	30.212 04ᵃ [20]	57.618 1ᵃ [20]	93.654 9ᵃ [20]	138.763 1ᵃ [20]	193.199 8ᵃ [20]	257.222 9ᵃ [20]	331.036 4ᵃ [20]	414.890 0ᵃ [20]
p_i^4	629.120 [21]	2 165.03 [23]	5 542.1ᵃ [25]	11 878ᵃ [25]	22 550ᵃ [25]	39 251ᵃ [25]	63 873ᵃ [25]	98 719.06 [26]
r_{ij}	8.668 427 [20]							
r_{ij}^{-1}	2.198 211 [19]							
r_{ij}^{-2}								
r_{ij}^2	36.848 09 [19]							
$\nabla_i * \nabla_j$	−0.301 846 7 [19]							
$\langle \delta(r_i) \rangle$	13.841 82 [19]							

ᵃSCF calculation.

on the local energy and is probably well represented in the trial wave function through the variance minimization. The latter, however, contributes to the variance only when two electrons of opposite spin are close. It is probable that same spin electrons need no explicit electron correlations since such correlations are already present in the antisymmetric part of the wave function. Such distinctions are not possible in the current trial wave function form. In view of our results, we suspect that $s-s$ antiparallel interactions are larger than $s-p$ antiparallel interactions which in turn are larger than $p-p$ antiparallel interactions. This feature will cause problems with other properties which depend on two close electrons. For this reason our values for r_{ij}^{-2} should be considered suspect for those systems with p-type orbitals. In contrast, all properties which depend on well separated electrons (the energy, r_i^{-1}, r_i^{-2}, r_{ij}, r_{ij}^2, etc.) should be accurate.

Although we use the same wave functions as Schmidt and Moskowitz and are in substantial agreement with their results, the total atomic energies listed in Table II have several noticeable differences with those reported in Refs. 10 and 15. In general our values are lower (i.e., closer to the exact nonrelativistic estimates) and have larger variances. The most likely reason for this is that Schmidt and Moskowitz use the Markov Chain method to generate each configuration (and so each is very similar to the next) whereas we use the biased selection method to generate them from an importance function (and so each is statistically independent). Because Schmidt and Moskowitz do not give the exact number of configurations used to evaluate their expectation values, a direct comparison with our variances cannot be made. The biased selection method, however, has previously been shown to adequately sample both the region near the nucleus and at the edge of the wave function.[11,13,14] The former undoubtedly accounts for our lower energy while the latter gives a more accurate estimate of its statistical error.

IV. CONCLUSIONS

Using the trial wave function form developed by Schmidt and Moskowitz, we have computed a number of properties for atoms He–Ne. For those properties which sample the valence region, our results are in good agreement with previous calculations (where available). Because of a defect in the wave function form, those properties which sample electrons being in close proximity are in substantial error. These can be probably corrected by distinguishing between the s and p-type orbitals and electrons of different spin.

In this paper we have also developed an improved method of generating configurations for systems with many electrons. Although we have only tested this procedure on systems up to ten electrons, our results suggest it could easily be extended to larger systems. Such a capability, when combined with the use of improved wave function forms, would enable the properties of a large number of interesting systems to be accurately determined.

ACKNOWLEDGMENTS

APPENDIX: OPTIMIZATION OF THE GUIDING FUNCTION

In an earlier paper we showed that the choice of guiding function could have a dramatic effect on the number of configurations needed to accurately estimate Eqs. (1) and (2).[14] For this reason, we developed a method of optimizing the form of the guiding function so as to minimize Eq. (2). Previously we took $g(r)$ to be a set of points connected by a line, i.e., a linear spline. By choosing the height, position, and number of these points, this form can approximate almost any function. A linear form, however, is difficult to optimize because additional points must frequently be introduced and each new point requires a new optimization of the heights of all points. Since the guiding function need only be positive definite and easily computable, we choose for the present calculations the form

$$g(r) = \exp\left[-\alpha * r + \sum_{k=1} a_k e^{-((r-b_k)/c_k)^2}\right]. \tag{A1}$$

This function is a good approximation of the general behavior of Ψ^2 with bumps at roughly each electron shell. For the atoms He–Ne we find that no more than four parameters (1 bump) are needed to define $g(r)$. The resulting calculations optimize quickly and are as accurate as those computed with a linear spline.

[1] R. L. Coldwell, Int. J. Quantum Chem. **S11**, 215 (1977).

[2] R. L. Coldwell and R. E. Lowther, Int. J. Quantum Chem. **S12**, 329 (1978).

[3] R. L. Coldwell, Int. J. Quantum Chem. **S13**, 705 (1979).

[4] R. E. Lowther and R. L. Coldwell, Phys. Rev. A **22**, 14 (1980).

[5] J. W. Moskowitz and M. H. Kalos, Int. J. Quantum Chem. **20**, 1107 (1981).

[6] J. W. Moskowitz, K. E. Schmidt, M. A. Lee, and M. H. Kalos, J. Chem. Phys. **76**, 1064 (1982).

[7] C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, Phys. Rev. Lett. **60**, 1719 (1988).

[8] C. J. Umrigar, Int. J. Quantum Chem. **S23**, 217 (1989).

[9] Z. Sun, S. Y. Huang, R. N. Barnett, and W. A. Lester Jr., J. Chem. Phys. **93**, 3326 (1990).

[10] K. E. Schmidt and J. W. Moskowitz, J. Chem. Phys. **93**, 4172 (1990).

[11] S. A. Alexander, R. L. Coldwell, H. J. Monkhorst, and J. D. Morgan III, J. Chem. Phys. **95**, 6622 (1991).

[12] G. Aissing, Phys. Rev. A **44**, R2765 (1991).

[13] S. A. Alexander, R. L. Coldwell, G. Aissing, and A. J. Thakkar, Int. J. Quantum Chem. **S26**, 213 (1992).

[14] S. A. Alexander, R. L. Coldwell, and J. D. Morgan III, J. Chem. Phys. **97**, 8407 (1992).

[15] K. E. Schmidt and J. W. Moskowitz, J. Chem. Phys. **97**, 3382 (1992).

[16] Z. Sun, W. A. Lester Jr. and B. L. Hammond, J. Chem. Phys. **97**, 7585 (1992).

[17] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[18] D. K. McKenzie and G. W. F. Drake, Phys. Rev. A **44**, R6973 (1991).

[19] F. W. King, Phys. Rev. A **40**, 1735 (1989).

[20] C. F. Bunge, J. A. Barrientos, and A. V. Bunge, At. Data Nucl. Data Tables **53**, 113 (1993).

[21] R. O. Esquivel, A. N. Tripathi, R. P. Sagar, and V. H. Smith Jr., J. Phys. B **25**, 2925 (1992).

[22] Sundholm and Olsen (unpublished result). Value cited in A. M. Martensson-Pendrill, S. A. Alexander, L. Adamowicz, N. Oliphant, J. Olsen, P. Oster, H. M. Quiney, S. Salomonson, and D. Sundholm, Phys. Rev. A **43**, 3355 (1991).

[23] A. N. Tripathi, R. P. Sagar, R. O. Esquivel, and V. H. Smith Jr., Phys. Rev. A **45**, 4385 (1992).

[24] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fisher, Phys. Rev. A **47**, 3649 (1993).

[25] S. R. Gadre, S. P. Gejji, and S. J. Chakravorty, At. Data Nucl. Data Tables **28**, 477 (1983).

[26] A. N. Tripathi, R. P. Sagar, R. Esquivel, and V. H. Smith, Jr. (to be published).