Quantum Monte Carlo determination of the lithium $2\,^2S \rightarrow 2\,^2P$ oscillator strength: Higher precision

R. N. Barnett, E. M. Johnson,* and W. A. Lester, Jr.

*Chemical Sciences Division, Lawrence Berkely Laboratory and Department of Chemistry,
University of California, Berkeley, California 94720*

(Received 17 June 1994)

We employ a quantum Monte Carlo method for the oscillator strength to the computation of the controversial $2\,^2S \rightarrow 2\,^2P$ transition of the Li atom. We use simple trial functions that are optimized for accuracy in coordinate expectation values as well as the energy. We obtain an oscillator strength of 0.7431(6), in very good agreement with the experimental value of 0.7416(12) [A. Gaupp, P. Kuske, and H. J. Andrä, Phys. Rev. A **26**, 3351 (1982)]. The precision obtained here, an order of magnitude greater than that of our previous value [R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., Int. J. Quantum Chem. **42**, 837 (1992)] shows that the quantum Monte Carlo oscillator strength unambiguously supports the experimental value over recent theoretical values.

PACS number(s): 32.70.Cs, 03.65.Ge, 02.70.Lq, 31.15.Ar

I. INTRODUCTION

Accurate calculation of the oscillator strength has proved difficult because of the need for highly sophisticated correlated wave functions [1]. Wave functions that yield excellent energies typically yield oscillator strengths of lower quality. This presents a special difficulty because wave functions are generally obtained by optimizing the energy expectation value. An excellent example of the difficulty facing theoretical approaches is the computation of the oscillator strength of the $2\,^2S \rightarrow 2\,^2P$ transition in lithium atom. A very precise experimental determination has been obtained [2], and recently a number of highly correlated theoretical calculations have been performed [3-6]. Despite these efforts, a sizable discrepancy between recent theoretical and experimental values persists. An exception to this disagreement can be found in the quantum Monte Carlo (QMC) computation of the oscillator strength by Barnett, Reynolds, and Lester [7]. In this study, excellent agreement between the mean of the QMC oscillator strength and experiment was obtained. The large statistical uncertainty of the computation, however, precluded critical comparison. A more precise QMC value could contribute substantively to understanding the requirements for the computation of accurate oscillator strengths.

The QMC method [8], in general, differs fundamentally from the variational and perturbative expansion methods referred to above. To obtain a transition dipole moment or an oscillator strength, the QMC approach we introduced to compute single-state expectation values of coordinate operators [9] is modified to compute two-state expectation values [10]. One advantage of the QMC method is that computed values, depending only on the nodes of a trial wave function, are much less sensitive to

the one- and N-particle expansions of the trial functions. It is also significant that QMC solutions are eigenfunctions of the Hamiltonian, a property that enforces local accuracy. The QMC solution is accurate in regions that can be of lesser importance for the determination of the energy, but may be crucial for obtaining an oscillator strength of high quality.

In our earlier study [7], agreement with the experimental value was suggested, but it was not conclusive. Here we introduce a modified approach to the computation of QMC oscillator strengths. This approach makes possible higher precision in order to provide further insight into this discrepancy between experiment and other recently computed oscillator strengths of high accuracy for the subject transition. Section II summarizes the method followed for the calculations reported here. (A thorough discussion of the approach is given in Ref. [10].) Section III presents our results and compares them with experimental and recent *ab initio* values. Section IV contains our conclusions.

II. QMC COMPUTATION OF THE OSCILLATOR STRENGTH

Energies are readily computed by QMC methods. (The algorithm we employ for this purpose is given in detail by Reynolds *et al.* [8b].) For the energy, only the distribution $\Psi_T \phi$ is needed; Ψ_T is a trial function describing the desired state and ϕ is the corresponding eigenfunction. To compute a transition moment or oscillator strength requires the distribution $\phi_1 \phi_2$. Here this is accomplished by employing a variational Monte Carlo (VMC) walk with QMC side walks [10]. The VMC walk samples the distribution $|\Psi_g|^2$, and the QMC walks, which begin with points sampled from the VMC distribution, sample values of ϕ_1/Ψ_{T_1} and ϕ_2/Ψ_{T_2}. The result is that the length form of the transition dipole moment can be computed as an average over the guiding function $|\Psi_g|^2$, and takes the form

*Present address: Phyto Pharmaceuticals Inc., 8876 Industrial Road, San Carlos, CA 94070.

     <u>51</u>   2049

$$\left\langle \phi_1 \left| \sum_i \mathbf{r}_i \right| \phi_2 \right\rangle$$

$$= \int |\Psi_g|^2 \frac{\phi_1}{\Psi_{T_1}} \left[\frac{\Psi_{T_1} \sum_i \mathbf{r}_i \Psi_{T_2}}{|\Psi_g|^2} \right] \frac{\phi_2}{\Psi_{T_2}} d\mathbf{R} \ . \qquad (1)$$

The choice of the guiding function, Ψ_g, is dictated by the need to sample values of ϕ/Ψ_T for both states. An obvious (and useful) choice is

$$\Psi_g = \sqrt{c_1^2 |\Psi_{T_1}|^2 + c_2^2 |\Psi_{T_2}|^2} \ , \qquad (2)$$

where we have set $c_1 \approx c_2$ in the calculations described below. Alternative choices of c_1 and c_2 are useful when one of the states is slowly convergent.

To evaluate Eq. (1), we sample the ratio $\phi(\mathbf{R})/\Psi_T(\mathbf{R})$ by sampling the function

$$P(\mathbf{R},t) = \exp[-t(E - E_R)] \langle \phi | \Psi_T \rangle \phi(\mathbf{R})/\Psi_T(\mathbf{R}) \ , \qquad (3)$$

where t is the propagation time of the QMC side walk, E is the QMC energy, and E_R is a reference energy chosen close to E to minimize the time dependence of P. For sufficiently large t, $P(\mathbf{R},t)$ is the number of walkers originating from the point $\mathbf{R}$ after propagation by a QMC algorithm for imaginary time t. If one value of P is sampled for each value of $\mathbf{R}$, the time dependence and the overlap integral must be explicitly computed during the QMC side walk. Alternatively, if two values of $P(\mathbf{R},t)$ are sampled, the product of the time dependence and the overlap integral can be computed from an average containing products of each pair of values of P. We computed the transition dipole moment based on both single and double samplings of P. This contrasts with our previous study, in which only a single sampling was used [7]. (See Ref. [10] for further discussion.) In addition, the product of two independent samplings of P yields an unbiased estimate of $|\phi/\Psi_T|^2$, while the square of a single sampling does not. Therefore, this product can be used to compute exact single-state expectation values, e.g., $\langle \phi | r | \phi \rangle$ [10]. Here we have used products of P to compute expectation values of r and r^2 over $|\phi|^2$ for each state.

Trial and guiding functions have essential roles in this approach. The trial functions Ψ_{T_1} and Ψ_{T_2} are chosen to describe the desired eigenstates. For each state, we choose $\Psi_T = \psi S$, where ψ is a Slater determinant and S is a correlation function explicitly dependent on electron-electron and electron-nucleus distances. We selected Weiss's basis set of near-Hartree-Fock quality which, as constructed, leads to Ψ satisfying the electron-nucleus cusp condition exactly [11]. This is highly desirable because it greatly reduces time-step bias in the QMC walks. The correlation function S was chosen to have the form

$$S = \exp \left[\sum_{i<j} \frac{ar_{ij}}{1 + br_{ij}} - \sum_i \frac{\lambda r_i^2}{1 + v r_i} \right] \ , \qquad (4)$$

where r_{ij} and r_i are electron-electron and electron-nucleus separations, respectively; and a, b, λ, and v are parameters. Since the electron-electron factor of Eq. (4), first term, expands the density well beyond that of the determinant alone, it is desirable to have a factor that moderates this effect, a purpose served by the second, electron-nucleus, term of Eq. (4). The latter term is quadratic, as opposed to linear, so that the cusp condition, exactly met by Weiss's basis set, remains satisfied.

The parameter a of Eq. (4) was set to 0.5 to satisfy the electron-electron cusp condition (for electrons of opposite spin). The remaining parameters were optimized, by hand, to minimize the energy with the constraint that the trial function expectation values $\langle r \rangle$ and $\langle r^2 \rangle$ remain close to our estimates of the exact values of these quantities. These estimates, or target values, were taken from our previous calculation [7]. The parameter values determined were $\lambda = 0.1$ and $v = 5$ for both states, and $b(^2S) = 2$ and $b(^2P) = 2.2$. In general, estimates of expectation values over $|\phi|^2$, for purposes of obtaining target values, are readily obtained in single-state calculations. In selecting the parameters, we found λ and v to have little effect on the energy, but to play a crucial role in obtaining good values for $\langle r \rangle$ and $\langle r^2 \rangle$.

The results of our previous calculations implied that convergence of the transition dipole moment correlated with convergence of $\langle r \rangle$ and $\langle r^2 \rangle$ for each state. We found that long QMC side walks were required to obtain converged values of these quantities because the trial functions, which lacked an electron-nucleus factor in S, yielded VMC expectation values that were quite large. We suspected that obtaining reasonable VMC values of $\langle r \rangle$ and $\langle r^2 \rangle$ for each state would increase the convergence rate of these quantities and the transition dipole moment in the QMC side walks.

III. RESULTS AND DISCUSSION

After optimizing trial function parameters with short VMC runs, we then performed larger VMC calculations for each state. Table I presents VMC results for the energy, $\langle r \rangle$, and $\langle r^2 \rangle$, and compares these with our previous calculation. For $\langle r \rangle$ and $\langle r^2 \rangle$, Table I shows that agreement with target values is now very good. In addition, the presence of the electron-nucleus correlation function, while not greatly affecting the energy, allows more flexibility in choosing b [see Eq. (4)], which results in a lower energy.

Table I also lists QMC energies (computed following the single-state algorithm of Ref. [8b]), and coordinate expectation values for each state (obtained following the procedure of Ref. [10]). The earlier QMC results of Barnett, Reynolds, and Lester [7] are in good accord with those computed here. The current QMC energies have been obtained by extrapolation to zero time step (τ), and all quantities now possess much greater precision. In addition to obtaining an unbiased estimate, extrapolation to $\tau = 0$ is useful in ascertaining bias for nonzero τ. In single-state calculations, we found that the time step used in the QMC side walks (0.010 hartree^{-1}) gave very little bias in the energy and no bias in the coordinate expectation values, even for the largest time step employed (0.030 for the ground state and 0.025 hartree^{-1} for the excited state).

The extrapolated QMC energies are in excellent agreement with estimated exact nonrelativistic Born-

TABLE I. Single-state expectation values. QMC coordinate expectation values are estimates of $\langle \phi | A | \phi \rangle$, $A \equiv r$, or r^2.

	$-E$(hartree^{-1})	$\langle r \rangle$ (bohr)	$\langle r^2 \rangle$ (bohr^2)
	$2\,^2S$		
Previous VMC[a]	7.4506(10)	1.6811(18)	6.247(14)
Current VMC	7.4608(01)	1.6670(05)	6.087(04)
Target		1.6610	6.104
Previous QMC[a]	7.478 09(24)	1.6610(66)	6.104(63)
Current QMC	7.478 00(10)	1.6604(05)	6.083(04)
Hylleraas [13]	7.478 059	1.6632	6.118
CI [4]	7.477 88		
Hylleraas [15]	7.478 059 5		
Hylleraas-CI [5]	7.478 060 1		
Hylleraas [12]	7.478 060 3		
Estimated exact [12]	7.478 060 3		
	$2\,^2P$		
Previous VMC[a]	7.3865(10)	1.9980(40)	9.703(45)
Current VMC	7.3915(01)	1.9499(08)	9.141(12)
Target		1.9510	9.210
Previous QMC[a]	7.410 31(22)	1.951(10)	9.21(12)
Current QMC	7.410 01(10)	1.9468(8)	9.170(12)
CI [4]	7.409 97		
Hylleraas-CI [5]	7.410 155 4		
Estimated exact [14]	7.410 16		

[a]Reference 7; for $\langle r \rangle$ and $\langle r^2 \rangle$, $t = 30$ hartree^{-1} values are employed.

TABLE II. Oscillator strengths for the $2\,^2S \rightarrow 2\,^2P$ transition of Li.

Recent *ab initio*	
MBPT [3]	0.7467
CI [4]	0.7478
MCHF [6]	0.7473
Hylleraas-CI [5]	0.7470
Previous VMC [7]	0.780(4)
Previous QMC [7]	0.7419(69)
This work	
VMC	0.7488(6)
QMC $t = 2.04$	0.7433(7)
QMC $t = 3.04$	0.7431(7)
QMC $t = 2.04$ Two P	0.7436(6)
QMC $t = 3.04$ Two P	0.7431(6)
Experimental	
Laser excitation [16]	0.7435(55)
Laser excitation [2]	0.7416(12)

Oppenheimer energies [12,14]. For the ground state, 99.9(2)% of the correlation energy is obtained (the number in parentheses is one standard deviation of the mean), and for the excited state 99.7(2)% is recovered. While the precision in the QMC energies is quite good, it is not at the level of recent expansion approaches, cf. Table I; we have uncertainty in the fourth decimal place. However, these are very accurate energies. There are further steps that can be taken to improve the precision of the QMC energy. However, for computing a transition dipole moment of high quality, this is not necessary.

Because of the improved efficiency gained from these trial functions, much higher precision in $\langle r \rangle$ and $\langle r^2 \rangle$ is obtained. Interestingly, this large increase in precision reveals values of $\langle r \rangle$ and $\langle r^2 \rangle$ that are slightly smaller than those estimated from large basis set expansion methods. Unfortunately, estimates of $\langle r \rangle$ and $\langle r^2 \rangle$ have not been reported in recent calculations of the excited state. We also computed $\langle z^2 \rangle$ for the excited state and obtained a QMC value for the quadrupole moment of 10.64(3) bohr^2, and note that it is slightly smaller than Pipin and Bishop's 10.82 bohr^2 [5].

Table II presents VMC and QMC oscillator strengths computed using the estimated exact energy difference of 0.067 90. The current VMC oscillator strength is seen to be substantially improved over our previous VMC value, even though the trial functions were not optimized for this quantity. In addition, the current VMC is in good agreement with the recent theoretical values in Table II. Therefore, the trial functions used here give an excellent starting point for shedding light on the discrepancy between theory and experiment.

We performed two computations of the QMC transition dipole moment; the convergence times (t) were 2.04 and 3.04 hartree^{-1}. For each computation, the transition dipole moment was evaluated at several t values, and we found rapid convergence of the transition dipole moment with little change occurring after 1.64 hartree^{-1}. The convergence times for each state were about 2 hartree^{-1}, a factor of 5 less than previously necessary [7]. The shorter convergence times increased efficiency in two ways: first, the QMC side walks, where most of the effort is concentrated, were much shorter; and, second, the correlation between the VMC and QMC transition dipole moments, which were computed simultaneously, was larger.

Table II gives oscillator strengths that resulted from the two convergence times. For each convergence time, the two entries are distinguished by whether an average or a product of the two values of P sampled for each point is used in computing the time dependence and overlap integral that enter into P; see Eq. (3). The consistency among the computed values is excellent. In addition, for the 3.04-hartree^{-1} computation, the differences between VMC and QMC transition dipole moments were unchanged after 2 hartree^{-1}. Of equal significance is the large reduction in the statistical error. More than an order-of-magnitude decrease, compared to the previous statistical error of 0.0069, has been obtained without a large increase in computational effort. Finally, the present oscillator strength of 0.7431(6) unequivocally supports the experimental value of 0.7416(12).

While the agreement with experiment is excellent, the present high precision precludes concordance with other recent high accuracy theoretical values that are in very good agreement with each other. Among these recent theoretical studies, the calculations of Weiss [4] are instructive because he examined the dependence of the oscillator strength on basis set size and degree of correlation. Three types of correlation were studied: single and double excitations, to describe intershell and intrashell correlations, and selected triple excitations. For each of

these, basis sets of up to $l=6$ were employed and appear to be exhaustive since no significant differences were observed beyond $l=3$. However, the effect of the type of correlation is noticeable. Adding selected triple excitations to the wave function yielded a decrease in the oscillator strength of 0.0019 to 0.7478. Furthermore, the discrepancy between the length and velocity forms of the oscillator strength increased from 0.0008 to 0.0020. Note that a change in the oscillator strength would have to be four times larger than the decrease caused by the selected triple excitations to give agreement with the upper bound of the experiment. In addition, the triples that are included bring the ionization energy to within 3 cm^{-1} of experiment. On this basis, better agreement with experiment, or QMC, upon including more triple excitations appears unlikely. However, such improvement cannot be ruled out, especially if an energy, or energy difference, is a poor indicator of the convergence of the oscillator strength. It would be interesting to know the fraction of triple excitations included by Weiss.

The results presented by Weiss are nearly conclusive in isolating which improvements to the wave function are required if better agreement with experiment and QMC is possible. The other recent theoretical studies, sometimes of impressive accuracy for single-state quantities [5], do not present an analysis of the kind given by Weiss [4]. However, some comparison between QMC and the basis-set-expansion approaches is useful. In the latter methods, wave-function parameters are chosen dominantly on the basis of energy optimization. Wave-function accuracy is lower in regions where contributions to the energy are less important. This holds regardless of basis set size. Finally, convergence of the energy, or other single-state quantities, as a measure of such accuracy can be mislead-

ing. (Unfortunately, as noted by Weiss [4], even the convergence behavior of computed oscillator strengths may also be misleading.)

The QMC method precedes quite differently. The QMC solution, an eigenfunction of the Hamiltonian, is determined in the approach used here by the nodes of the trial function employed. Within this constraint, all regions of space are treated equally and exactly. This is in contrast to expansion methods that approximate an eigenfunction, albeit one not constrained by nodal boundary conditions, to varying accuracy depending on the contribution to the energy.

IV. CONCLUSIONS

Calculations of the oscillator strength for the Li $2^2S \rightarrow 2^2P$ transition have been performed. Faster convergence in QMC side walks, achieved by improving single-state coordinate expectation values through simple improvements in the trial function, yields an oscillator strength that agrees with, and is more precise than, experiment. Statistical error has been reduced by an order of magnitude with the result that, while agreement with experiment is maintained, agreement with other recent *ab initio* approaches is not found.

[1] See, for example, the discussion in W. F. Chan, G. Cooper, and C. E. Brion, Phys. Rev. A **44**, 186 (1991).

[2] A. Gaupp, P. Kuske, and H. J. Andrä, Phys. Rev. A **26**, 3351 (1982).

[3] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **40**, 2233 (1989).

[4] A. Weiss, Can. J. Chem. **70**, 456 (1992).

[5] J. Pipin and D. M. Bishop, Phys. Rev. A **45**, 2736 (1992).

[6] T. Brage and C. Froese Fischer, Phys. Rev. A **49**, 2181 (1994).

[7] R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., Int. J. Quantum Chem. **42**, 837 (1992).

[8] (a) For reviews, see B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994); W. A. Lester, Jr. and B. L. Hammond, Annu. Rev. Phys.

Chem. **41**, 283 (1990); (b) P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, Jr., J. Chem. Phys. **77**, 5593 (1982).

[9] R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., J. Comp. Phys. **96**, 258 (1991).

[10] R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., J. Chem. Phys. **96**, 2141 (1992).

[11] A. Weiss, Astrophys. J. **138**, 1262 (1963).

[12] D. K. McKenzie and G. W. F. Drake, Phys. Rev. A **44**, 6973 (1991).

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

[14] T. Alhenius and S. Larsson, Phys. Rev. A **8**, 1 (1973).

[15] F. W. King and M. P. Bergsbaken, J. Chem. Phys. **93**, 2570 (1990).

[16] J. Carlsson and L. Sturesson, Z. Phys. D **14**, 281 (1989).