

# Quantum and variational Monte Carlo interaction potentials for $\text{Li}_2$ ( $X^1\Sigma_g^+$ )<sup>☆</sup>

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Optimized trial functions are used in quantum Monte Carlo and variational Monte Carlo calculations of the  $\text{Li}_2$  ( $X^1\Sigma_g^+$ ) potential curve. The trial functions used are a product of a Slater determinant of molecular orbitals multiplied by correlation functions of electron–nuclear and electron–electron separation. The parameters of the determinant and correlation functions are optimized simultaneously by reducing the deviations of the local energy  $E_L$  ( $E_L \equiv \Psi_T^{-1} H \Psi_T$ , where  $\Psi_T$  denotes a trial function) over a fixed sample. At the equilibrium separation, the variational Monte Carlo and quantum Monte Carlo methods recover 68% and 98% of the correlation energy, respectively. At other points on the curves, these methods yield similar accuracies.

## 1. Introduction

Potential energy curves and surfaces govern spectroscopy and collision dynamics. To be useful for computing quantities such as cross sections and spectroscopic constants, however, these surfaces should be determined to very high accuracy. Towards this end, accurate computations of the energy over a range of coordinates are required.

Within the last ten to fifteen years quantum Monte Carlo (QMC) approaches, for obtaining numerical solutions of the Schrödinger equation have yielded very accurate energies for small systems<sup>#1</sup>. In the diffusion QMC method with fixed nodes [1] (referred to as QMC hereafter), the trial function,  $\Psi_T$ ,

determines both the precision and accuracy of the QMC energy. Precision is determined by the smoothness of the local energy and accuracy is dictated by the quality of the nodal structure of  $\Psi_T$ . For these reasons, trial function optimization holds considerable interest in QMC.

Recently, an approach has appeared based on minimizing deviations of the local energy over fixed samples [3,4]. Since the optimization is performed over a fixed sample, random walks are eliminated allowing greater efficiency during nonlinear optimization.

The fixed-sample optimization approach is employed here to obtain trial functions at several widely spaced internuclear separations of ground state  $\text{Li}_2$  ( $X^1\Sigma_g^+$ ). With these trial functions, potential curves (PCs) can be computed following the VMC and QMC approaches.  $\text{Li}_2$  serves as an excellent test case because its potential curve has been well characterized theoretically [5–11] and experimentally [12–16].

In section 2 we describe the trial function and optimization algorithm. In section 3 we present optimized trial function parameters, VMC and QMC energies at several internuclear separations, and the resulting spectroscopic constants. The QMC computed curve is compared with one deduced from ex-

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<sup>#1</sup> For a review of work through 1990, see ref. [1]. Earlier reviews are provided by Schmidt and Kalos, ref. [2].

periment and the QMC spectroscopic constants are compared with previously computed values and experiment. Finally, the dissociative behavior of the VMC and QMC curves is investigated with computations at very large separation. Section 4 contains concluding remarks.

## 2. Trial function and optimization

In this study we employ a relatively simple trial function form. It consists of a product of two determinants of molecular orbitals (MOs) containing electrons of opposite spin, multiplied by a correlation function of electron–nuclear and electron–electron separations. The MOs,  $1\sigma_g$ ,  $1\sigma_u$  and  $2\sigma_g$ , for the ground state of  $\text{Li}_2$ , are linear combinations of  $1s$ ,  $2s$  and  $2p_x$  Slater orbitals centered on each atom. Symmetry restrictions on the MOs and trial function normalization yield six independent linear coefficients. Orbital exponents may also be varied, and, unlike conventional expansion techniques, different MOs may be constructed of STOs with different exponents. Here the first two MOs have identical orbital exponents, but those of the  $2\sigma_g$  are different, resulting in six exponents for optimization and greatly enhancing basis set flexibility.

The electron–electron correlation function,  $S_e$ , is chosen to have the form [17]

$$S_e(\{r_{ij}\}) = \exp\left(-b \sum_{ij} \exp(-ar_{ij})\right). \quad (1)$$

The parameter  $a$  is constrained to be  $0.5b$ . This constraint is useful in reducing the variance in the local energy,  $E_L \equiv \Psi_T^{-1} H \Psi_T$ , since it removes the singularity in  $E_L$  due to the coalescence of electrons of opposite spin. (Removing the singularity for electrons of like spin is not important for present purposes because  $\Psi_T \rightarrow 0$  as such electrons coalesce.) This correlation function is both easy to evaluate and yields a good description of electron correlation [17]. The electron–nuclear correlation function,  $S_n$ , further increases trial function flexibility and takes the familiar Jastrow form

$$S_n(\{r_{i\alpha}\}) = \exp\left(-\sum_{i,\alpha} \frac{\lambda r_{i\alpha}}{1 + \nu r_{i\alpha}}\right). \quad (2)$$

The total number of parameters to be optimized is 15: six linear coefficients, six exponents, in addition to  $b$  of  $S_e$ , and  $\lambda$  and  $\nu$  of  $S_n$ .

The trial function parameters are optimized by minimizing the sum of the deviations of local energies,  $V$ , where

$$V = \sum_{n=1}^N [E_L(R_n) - E_R]^2. \quad (3)$$

Here  $R_n$  specifies the positions of the electrons and these points are selected using VMC from the distribution  $|\Psi_0|^2$ , where  $\Psi_0$  is an initial trial function.  $E_R$  is a reference energy and  $N=1000$  in the calculations below. Trial function parameters are governed by  $E_R$ , the sample  $\{R_n\}$ ,  $\Psi_0$ , and the point at which optimization is assumed to be complete. Each of these factors is varied in the optimization procedure. (For a detailed description of the optimization procedure, see ref. [3].)

The first geometry considered was the experimental minimum energy separation (5.05 bohr) with SCF MOs for  $\Psi_0$ . For the remaining internuclear separations,  $\Psi_0$  is chosen as the trial function optimized at the previous separation.

## 3. Results and discussion

Optimized trial functions were obtained over the range of internuclear separations from 2.5 to 10.0 bohr. The resulting MO coefficients and exponents, and correlation function parameters are given in tables 1–3, respectively. For each of the internuclear separations at which an optimized trial function was determined, both VMC and QMC energies were computed; these are reported in table 3.

Once the trial function is specified, the most important requirement for QMC calculations is the removal of time-step bias [1]. To ascertain the bias of the present calculations, QMC energies were computed to high precision (statistical error  $\leq 0.0008$  h) over a range of time steps,  $0.0025 \leq \tau \leq 0.01$  (hartree) $^{-1}$ , at  $R=3.5$  and 5.05 bohr. Results of these computations are presented in figs. 1 and 2. At  $R_e$  (5.05 bohr), time-step bias is not statistically significant until  $\tau > 0.05$  (hartree) $^{-1}$ , and at  $R=3.5$  bohr this bias does not become apparent until  $\tau > 0.02$  (hartree) $^{-1}$ . Based on these results, we used a time

Table 1  
Optimized MO coefficients versus  $R$  <sup>a)</sup>

$R$ (bohr)	MO					
	$1\sigma_g$		$1\sigma_u$		$2\sigma_g$	
	$c(2s)$	$c(2p_z)$	$c(2s)$	$c(2p_z)$	$c(2s)$	$c(2p_z)$
2.500	0.4307	0.0182	0.4111	0.0436	0.4810	0.0703
3.000	0.4430	0.0206	0.4424	0.0171	0.3784	0.0793
3.500	0.4519	0.0137	0.4306	0.0096	0.4505	0.0947
4.000	0.3599	0.0005	0.3727	0.0099	0.2244	0.0269
4.500	0.3585	0.0011	0.3563	0.0004	1.1882	0.2460
5.050	0.3652	-0.0011	0.3306	0.0066	1.1646	0.2253
6.000	0.4734	0.0009	0.4728	0.0007	0.8848	0.1045
7.000	0.3563	-0.0055	0.3452	0.0014	0.5819	0.0402
8.500	0.4147	-0.0038	0.3462	-0.0016	0.2860	0.0419
10.000	0.3375	0.0009	0.3763	-0.0028	0.4096	0.0328

<sup>a)</sup> For the  $1\sigma_g$  and  $1\sigma_u$  MOs  $c(1s) = 1$ , and for the  $2\sigma_g$   $c(1s) = -0.1$ . Coefficients are given for the orbitals centered on the atom with the origin at  $(0, 0, -R/2)$ . All remaining coefficients can be obtained by symmetry.

Table 2  
Optimized exponents ( $\zeta$ )

$R$ (bohr)	MO					
	$1\sigma_g, 1\sigma_u$			$2\sigma_g$		
	$\zeta(1s)$	$\zeta(2s)$	$\zeta(2p_z)$	$\zeta(1s)$	$\zeta(2s)$	$\zeta(2p_z)$
2.500	3.5029	2.7593	2.6125	1.8922	0.7061	0.9837
3.000	3.5478	2.7854	2.9315	2.3658	0.7514	1.1180
3.500	3.5601	2.7847	2.7450	2.3650	0.7173	0.8276
4.000	3.4234	2.7001	3.1443	2.7570	0.6797	1.1521
4.500	3.4074	2.6871	1.3006	1.8382	0.7336	1.0049
5.050	3.4005	2.6665	2.4707	1.9649	0.7328	0.9892
6.000	3.6098	2.8421	3.1089	1.9876	0.7232	0.8283
7.000	3.4020	2.6650	2.7902	2.7170	0.6751	0.5555
8.500	3.4443	2.7189	2.8026	2.7594	0.5935	0.7129
10.000	3.4126	2.7107	2.8039	2.8660	0.5977	0.6120

step of  $0.010$  (hartree)<sup>-1</sup> for the other internuclear separations considered.

We first examine the quality of the computed energies by considering results at  $R_c$ . The optimized trial function at this separation yields a VMC energy of  $-14.9564(6)$  hartree while the QMC approach further improves the energy to  $-14.9923(7)$  hartree. From the Hartree-Fock (HF) energy of  $-14.872$  hartree <sup>#2</sup> and the estimated exact non-relativistic Born-Oppenheimer energy of  $-14.9945$  hartree

<sup>#2</sup> For the Hartree-Fock energy, see ref. [19].

[20], the VMC and QMC approaches recover 68.9(5)% and 98.2(8)% of the correlation energy, respectively. In a separate calculation, one of us [21] has computed a QMC energy for Li atom of  $-7.47809(24)$  hartree, the exact non-relativistic Born-Oppenheimer energy is  $-7.47807$  hartree [22], allowing a QMC estimate of  $D_c$  to be obtained. After correcting for finite mass, i.e. multiplying the energy by  $M/(M+m_e)$  where  $M$  is the  $Li_2$  mass, the QMC value of  $D_c$  is  $1.00(3)$  eV. This result is in good agreement with the experimental result of  $1.06$  eV [15,16].

Table 3  
Optimized correlation function parameters, VMC energies, and QMC energies versus  $R^a$

R	Parameter			Energy		
	$b$	$\lambda$	$\nu$	VMC <sup>b)</sup>	QMC <sup>b)</sup>	QMC <sup>c)</sup>
2.500	0.3765	-0.0276	4.1659	-14.8048(7)	-14.8480(11)	
3.000	0.3868	-0.0634	4.4632	-14.8723(5)	-14.9117(09)	-14.9069(7)
3.500	0.3994	-0.0843	4.4533	-14.9165(5)	-14.9522(08)	
4.000	0.3927	-0.1503	40.9298	-14.9372(6)	-14.9753(12)	
4.500	0.4012	-0.0788	40.9707	-14.9539(5)	-14.9877(09)	
5.050	0.3884	-0.0159	0.5754	-14.9564(6)	-14.9919(07)	-14.9876(6)
6.000	0.3910	-0.0646	2.2927	-14.9507(6)	-14.9860(09)	
7.000	0.3869	-0.0222	4.4623	-14.9397(5)	-14.9783(08)	-14.9775(5)
8.500	0.3886	-0.0217	4.4755	-14.9241(5)	-14.9651(10)	
10.000	0.4142	-0.0001	4.4754	-14.9099(5)	-14.9592(09)	

<sup>a)</sup> Energies are in hartree and distances in bohr. In tables 3-5, numbers in parentheses are one standard deviation in the mean.

<sup>b)</sup> This work; QMC are energies computed at  $\tau=0.01$  (hartree)<sup>-1</sup>.

<sup>c)</sup> With  $\Psi_{11}$  of ref. [18]; energies computed at  $\tau=0.01$  (hartree)<sup>-1</sup>.

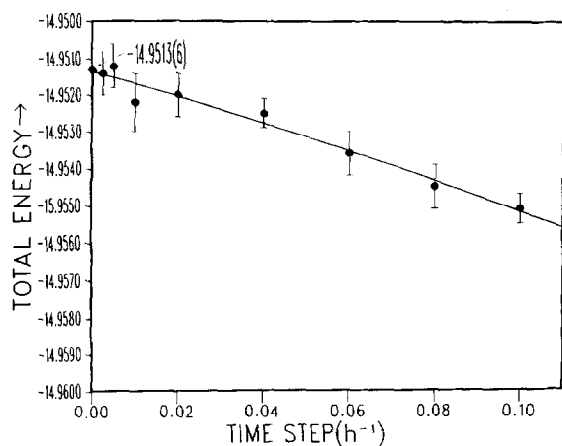


Fig. 1. The QMC energy versus time step at  $R=3.5$  bohr.

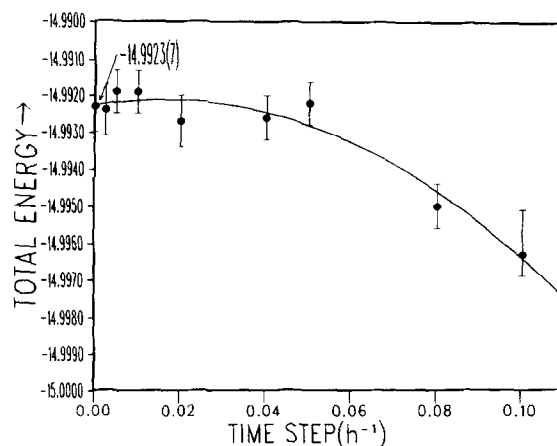


Fig. 2. The QMC energy versus time step at  $R=R_c$  (5.05 bohr).

Spectroscopic constants extracted from our calculated PC are listed in table 4 and compared to previous results. The mean values and statistical errors in our reported spectroscopic constants were obtained from the computed Monte Carlo energies as follows. At each separation studied, an energy was sampled from a Gaussian distribution with Monte Carlo-computed mean and standard deviation listed in table 3. The mean values of  $R_c$  and  $E(R_c)$  were determined from a sixth-order polynomial fit of the selected energies over the range of 2.5 to 7.0 bohr. The remaining constants were obtained from a standard Dunham analysis employing the expression

$$\begin{aligned} \Delta(r) &= E(r) - E(R_c) \\ &= r^2(a_0 + a_1 r + a_2 r^2 + a_3 r^3), \end{aligned} \quad (4)$$

for  $3 \leq R \leq 10$  bohr with  $r = (R - R_c)/R_c$ . A new set of energies was then sampled, constants computed, and the procedure repeated until the means and standard deviations of the quantities reported in table 4 were determined to high precision.

The VMC and QMC energies are either among the lowest or are the lowest, computed by ab initio methods, see table 4. Monte Carlo values are somewhat less accurate, relative to experiment, than the best ab initio results. Also, quantities which are most sen-

Table 4  
Total energies at  $R_e$  and spectroscopic constants of  $\text{Li}_2$  ( $X^1\Sigma_g^+$ )

Ref.	Method	$E$ (hartree)	$R_e$ (bohr)	$D_e$ (eV)	$\omega_e$ ( $\text{cm}^{-1}$ )	$\omega_e x_e$ ( $\text{cm}^{-1}$ )	$\alpha_e$ ( $\text{cm}^{-1}$ )
6			5.009	1.053	352.4	3.66	
			5.003	1.080	356.9	3.66	
7	MCSCF		5.107	0.893	335.2	2.64	0.0073
	val. CI		5.092	1.037	347.4	2.54	0.0070
	MC/CI		5.047	1.012	350.5	2.58	0.0070
	JSTS		5.056	1.001	351.9	2.56	0.0073
8	MCSCF	-14.8977	5.094	0.880	339.5	2.64	0.0078
	MCCI-2	-14.9622	5.117	0.920	342.7	2.60	0.0078
	MCCI-4	-14.9652	5.058	1.000	351.9	2.56	0.0073
9		-14.9032	5.088	1.029	347.1	3.60	
		-14.9652	5.085	1.013	348.5	3.70	
this work	VMC	-14.9571(7)	5.12(6)		382(10)	2.60(41)	0.0052(12)
	QMC	-14.9931(10)	5.16(9)	1.00(3)	366(17)	2.72(71)	0.0056(20)
12	exp.	-14.9945 <sup>a)</sup>	5.051	1.057 <sup>b)</sup>	351.4	2.61	0.0068
				1.056 <sup>c)</sup>			

<sup>a)</sup> Estimated exact non-relativistic Born-Oppenheimer energy, ref. [20]. <sup>b)</sup> Ref. [15]. <sup>c)</sup> Ref. [16].

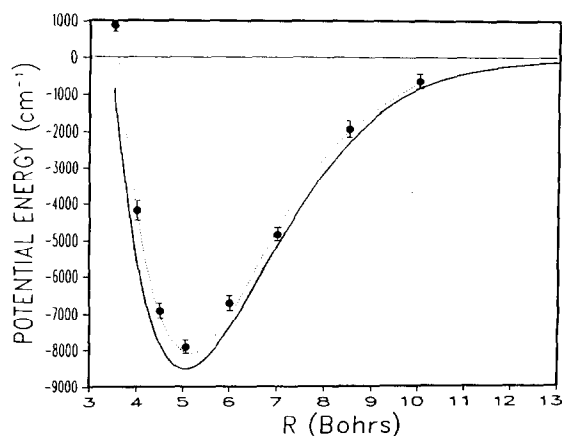


Fig. 3. QMC potential energy curve of  $\text{Li}_2$ . The solid curve is deduced from experiment, see ref. [15].

sitive to the shape of the PC,  $\omega_e x_e$  and  $\alpha_e$ , are found to possess large statistical errors. Therefore, while agreement with experiment is reasonable, and perhaps encouraging (fig. 3), the overall quality is generally beneath that of the other ab initio approaches.

Finally, we consider trial function optimization and the subsequent computation of VMC and QMC energies at large separations. As is well known, a single-determinant trial function does not dissociate to

two ground-state Li atoms. Instead, in the asymptotic limit our trial function consists of equal representations of the  $\text{Li}^- - \text{Li}^+$  and neutral ground states. Therefore, the correct representation of the "ionic" and "neutral" components of the trial function is required in the fixed sample to correctly integrate over  $|\Psi_0|^2$ . Since points representing these components are easily discerned at large  $R$  by counting the number of electrons around each atom, a fixed sample of high quality is readily obtained. In the guided VMC walk employed here [18], walkers may infrequently cross regions where  $|\Psi|^2$  is small. At large  $R$ , we have observed little interchange between ionic and neutral configurations causing convergence from an incorrect proportion of ionic versus neutral to be time consuming. Therefore, a 50% ionic / 50% neutral ensemble is employed to start VMC calculations.

For the optimization at  $R=30$  bohr, we selected 1150 points from  $|\Psi_0|^2$ . We then minimized deviations of the local energy about a reference energy  $E_R = -14.900$  hartree – the estimated exact energy of two Li atoms is  $-14.956$  hartree. The variance,  $V$ , is reduced from an initial value of 1.25 to  $0.10$  ( $\text{hartree})^2$ . The resulting VMC energy is  $-14.884(1)$  hartree corresponding to recovery of 20% of the correlation energy, exact and Hartree–

Table 5  
Li<sub>2</sub> QMC energies.  $R=30$  bohr

$\tau$ (hartree) <sup>-1</sup>	$-E$ (hartree)
0.010	14.960(3)
0.005	14.957(2)
0.002	14.954(2)
0.001	14.960(2)
$2E_{\text{QMC}}(\text{Li})$	14.956(1)
$2E_{\text{exact}}(\text{Li})$	14.956

Fock are taken as twice the atomic energies. This value is far below the accuracy obtained with VMC at the minimum-energy separation where 69% of the correlation energy is recovered and is due to improper trial function dissociation.

Table 5 lists QMC energies computed at 30 bohr over a range of time steps. We see from the good agreement between the computed energies that time-step bias lies beneath the statistical error. Most satisfying is the excellent agreement between Li<sub>2</sub> QMC energy and the estimated exact asymptotic value of  $-14.956$  hartree for two isolated ground-state atoms confirming proper dissociation of the QMC PC – despite the presumed inappropriateness of the trial function in this region. This result is readily explained. The ionic part of the trial function represents a highly excited state and, as such, is rapidly removed by the QMC walk which converges to the ground (neutral) state and a statistically exact energy.

#### 4. Concluding remarks

The VMC and QMC potential curves reported here both yield spectroscopic constants in reasonable agreement with ab initio and recent experimental values. We note that the VMC and QMC results agree statistically. Although QMC recovers a significantly greater portion of the correlation energy than VMC ( $\approx 30\%$  at  $R_c$ ), no significant improvement in the PC is obtained. This may be due, in part, to the large statistical errors of the spectroscopic constants. However, the trial function, a single Slater determinant multiplied by simple correlation functions, may be readily improved. Efforts along these lines should yield large reductions in statistical error and an improved PC.

As a final point, we note that the QMC walk eliminates the ionic component of a single-reference trial function and reproduces the exact asymptotic energy at large separation. Even though the trial function does not dissociate properly, our QMC PC yields the correct asymptotic behavior.

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