

## ARTICLES

**Pseudopotential variational quantum Monte Carlo approach to bcc lithium**

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The pseudopotential variational quantum Monte Carlo scheme is applied to bcc lithium. The pseudopotential is constructed from all-electron Hartree-Fock calculations. Atomic levels calculated using the pseudopotential show good agreement with experimental atomic spectroscopic data. Calculations for bcc lithium provide accurate equilibrium lattice constant and bulk modulus. Calculated cohesive energy is within 0.1 eV of the experimental value. Use of the pseudopotential enables accurate evaluation of the correlation energy among the conduction electrons. The results have demonstrated that the correlation energy is very important in determining bulk lithium properties. [S0163-1829(96)04135-5]

As one of the simplest metals, lithium was regarded as a free-electron system. Extensive researches, however, have shown that the anisotropy of its Fermi surface is more pronounced than other alkali metals<sup>1</sup> and electron-electron and electron-phonon interactions are relatively strong.<sup>1,2</sup> Lithium, like other alkali metals, forms a bcc structure at room temperature, but it has a phase transformation around 70 K and exhibits a close-packed structure at low temperatures.<sup>3</sup> The interests in the ground-state structure of Li surged after Overhauser suggested<sup>4</sup> that its low-temperature phase had a complex rhombohedral 9R structure. Later this suggestion was verified by the neutron-scattering data.<sup>5,6</sup> The low transition temperature indicates that the energy difference between the bcc and the 9R phase should be on the order of 5 meV. Theoretical calculations have obtained results ranging from 80 meV (Ref. 7) to about 1 meV.<sup>1</sup> Recently, Sakurai *et al.* reported<sup>8</sup> high-resolution Compton profile of bcc Li measured by synchrotron radiation. The results again showed significant differences between bcc Li and a free-electron system. The anisotropy of the Fermi surface is in good agreement with accurate local-density approximation (LDA) band calculations. The momentum distribution, however, showed a pronounced departure from the conventional single-particle picture, especially at small wave vectors.<sup>8</sup>

In this paper we report calculations of bcc Li using the pseudopotential variational quantum Monte Carlo (QMC) method.<sup>9</sup> Basically, this method uses no approximation other than the pseudopotential and the search for the optimal variational parameters is guided by the variational principle. The objective of this study is to focus on the conduction electrons and to calculate lattice properties using the variational QMC method. Our goal is to use lattice properties to aid the search for an accurate many-electron wave function. This wave function can then be used in the future to calculate momentum distribution and other quantities that are inaccessible by any of the single-particle approaches.

There have been numerous theoretical calculations of bcc Li in the past ten years. The majority of the calculations are based on the successful LDA scheme of the density-

functional theory.<sup>10</sup> The first diffusion QMC calculation on bcc Li (Ref. 11) obtained a cohesive energy of 1.09 eV, which is 0.56 eV smaller than the experimental value of 1.65 eV. A recent variational calculation<sup>12</sup> obtained a similar cohesive energy. In general, LDA calculations tend to overestimate the cohesive energy. An all-electron LDA study on alkali metals<sup>13</sup> reported a 2.03 eV cohesive energy for bcc Li. After being corrected with the spin polarization energy of the Li atom, the cohesive energy became 1.81 eV. Our own pseudopotential LDA calculation obtained 1.82 eV.

The theoretical lattice constant of bcc Li is also the topic of much discussion. Results from variational QMC calculations<sup>11,12</sup> were larger than the experimental value of 6.57 bohrs (Ref. 14) by 2–3%. The diffusion QMC result of 6.9 bohrs (Ref. 11) was almost 5% larger than the experimental result. Hartree-Fock (HF) calculations,<sup>15</sup> depending on the basis set, have obtained results that are as much as 7% larger than the experimental value. LDA calculations, on the other hand, have found<sup>13</sup> a lattice constant that is 3% smaller than that of the experiment. However, an improved gradient expansion LDA scheme<sup>16</sup> has obtained a lattice constant that is in good agreement with that of the experiment.

The bulk modulus is directly related to the second-order derivative of the total energy with respect to the lattice constant. For a bcc structure, it is  $-2b/9a_0$ . Here  $b$  is the second-order derivative taken at the total-energy minimum and  $a_0$  is the equilibrium lattice constant. The theoretical bulk modulus is known to be very sensitive to approximations and other factors of the calculation. The measured bulk modulus for bcc Li is 130 kbar.<sup>17</sup> The result from a recent variational QMC calculation<sup>12</sup> was 25% higher. Part of the difficulty in obtaining a reliable bulk modulus is the numerical noise in QMC calculations. The result from HF calculations<sup>15</sup> differs from the experimental value by a factor of 2. Several LDA results<sup>13,16</sup> are about 15% higher than the experimental value.

The total energy of the Li atom is  $-203.43$  eV.<sup>18</sup> With a cohesive energy of 1.65 eV, the total energy of the Li bcc

crystal becomes  $-205.08$  eV per atom. Considering the HF total energy of  $-202.77$  eV,<sup>15</sup> one obtains 2.31 eV as the total correlation energy of bcc Li. A recent variational QMC calculation<sup>12</sup> has obtained 1.7 eV. Although this is 73% of the total correlation energy, the remaining 0.5 eV accounts for 1/3 of the cohesive energy. It is interesting to note that the Li atom has a 1.24 eV correlation energy.<sup>19</sup> If we assume that the intra-atomic correlation of bcc Li is similar to that of the Li atom, we can conclude that the interatomic correlation in bcc Li is about 1 eV, almost as strong as the intra-atomic correlation.

Our major motivation for using the pseudopotential is to reduce the fluctuation in energies of the core electrons. The difficulty of treating the core electrons is the main obstacle that hinders the application of QMC methods to real materials. With pseudopotentials, only the chemically active valence electrons are treated in the calculations and the atomic numbers are effectively reduced. Also, it is conceivable that the core electron correlation and valence electron correlation are very different, so a simple correlation factor cannot be equally effective for both the core and the valence electrons. Since the success of the variational QMC method largely depends on one's ability to employ a trial wave function that is simple yet captures the main feature of correlation, the use of a pseudopotential is particularly beneficial for variational QMC calculations. As our results will demonstrate, the use of a pseudopotential enables us to employ a simple correlation function to capture almost all of the correlation energy without a large number of variational parameters. Finally, the use of a pseudopotential will lead to smoother charge densities, which in turn, will lead to better LDA single-particle wave functions that are used in the trial wave function. Earlier application of the pseudopotential variational QMC method to diamond and silicon crystal<sup>9</sup> have achieved satisfactory results.

The details of this method have been reported earlier.<sup>9</sup> Briefly, the Hamiltonian for the electrons contains the kinetic energy, the potential energy due to pseudopotentials, and the interelectron Coulomb interaction. No spin-dependent interaction term is included since the spin-orbit interaction is negligible for lithium. The trial wave function has the form

$$\Psi(\mathbf{R}) = \Psi_J(\mathbf{R})D^\uparrow(\mathbf{R})D^\downarrow(\mathbf{R}), \quad (1)$$

where  $\mathbf{R}$  is the coordinate in  $3N$  space. The antisymmetrical Slater determinant  $D$  is formed by single-particle wave functions that are solutions of effective LDA Kohn-Sham equation.<sup>10</sup> The Slater determinants for the up and the down spin are of the same rank and contain no variational parameter. The symmetric wave function  $\Psi_J$  contains a usual Jastrow-type two-body term  $u$  and an additional one-body term  $\chi$  as

$$\Psi_J(\mathbf{R}) = \exp\left(\sum \chi_\sigma(\mathbf{r}_i) - \sum u_{\sigma\sigma'}(r_{ij})\right), \quad (2)$$

where  $\sigma$  and  $\sigma'$  are spin indices and the sum is over all electrons in the simulation cell. The expectation value of total energy, defined as

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (3)$$

is then evaluated using the Metropolis algorithm.<sup>20</sup> The optimal variational parameters are searched and determined by the lowest total energy.

A simple, standard form of Jastrow factor is chosen for the calculation:

$$u(r) = \frac{A}{r} [1 - \exp(-r/F)], \quad (4)$$

where  $A$  is a variational parameter and  $F$  is determined by the ‘‘cusp’’ conditions for parallel and antiparallel spins. For a uniform electron gas, it can be shown<sup>21</sup> that the long-range behavior of the  $u$  term is determined by the electron density. We use the value of  $A$  for the uniform electron gas as the starting point for the variational search. It is easy to see that the effect of the Jastrow factor is to suppress the wave function amplitude whenever two electrons are near each other. Our previous studies<sup>9</sup> have shown that in contrast to a uniform electron gas, for real materials, the  $u$  term will dilute the high electronic density near the nucleus.

A one-body term  $\chi$  is introduced in the present scheme to restore the charge density altered by the  $u$  term and to give another variational degree of freedom. The  $\chi$  term is determined numerically by

$$\chi(\mathbf{r}) = \frac{\alpha}{2} \ln[\rho(\mathbf{r})_{u=0} / \rho(\mathbf{r})_{u \neq 0}], \quad (5)$$

where the variational parameter  $\alpha$  is an overall scaling factor. It can be seen from the design of the  $\chi$  term that the purpose is to constrain the charge density to the HF results. Earlier results<sup>9</sup> have shown that inclusion of the  $\chi$  term is more important for highly nonuniform systems such as atoms than for solids.

The pseudopotential for Li is generated from both the standard LDA calculation and the restricted Hartree-Fock atomic calculation. The calculations are performed on the  $2s^{0.5}2p^{0.1}$  configuration. A method by Kerker<sup>22</sup> is used to generate the norm-conserved nonlocal pseudopotential for  $2s$  and  $2p$  with a radius of 2.5 bohrs. The smallest interatomic distance used in this study is 5.4 bohrs. We have also tried the local pseudopotential generated from the  $2s^1$  configuration. Tests, however, showed that purely local pseudopotential is of poor quality.

To test the transferability of the pseudopotential, LDA all-electron and pseudopotential calculations are performed for different atomic states. The results are summarized in the first two rows of Table I. It can be seen that the errors introduced by the pseudopotential are about 0.03 eV. Of course, the agreement between the first two rows of Table I does not address the concern that the pseudopotentials derived from LDA or HF calculations may not be justifiably used in variational QMC calculations. At present, there is no general criterion to directly test the applicability. However, since the pseudolithium atom has only one electron, the pseudopotential can be tested by a direct comparison between the experimental atomic spectroscopic data<sup>18</sup> with the exact solution of the Schrödinger equation.

The test results are also listed in Table I. The two rows labeled ‘‘exact’’ are numerical solutions of the one-electron Schrödinger equation using either the LDA or the HF pseudopotential. The agreement with experiments is consis-

TABLE I. Pseudopotential tests. Binding energies are in units of eV and relative to  $\text{Li}^+$ . LDA calculations are spin polarized with the Ceperley-Alder exchange correlation. The  $3d^1$  state is calculated with the  $s$  pseudopotential and using the  $p$  pseudopotential causes less than 2 meV differences.

Method	$2s^1$	$3s^1$	$4s^1$	$2p^1$	$3p^1$	$3d^1$
LDA all-electron	5.47	2.21	1.20	3.66	1.77	1.58
LDA pseudopotential	5.44	2.18	1.18	3.62	1.73	1.58
exact (LDA)	5.51	2.05	1.06	3.67	1.60	1.51
exact (HF)	5.34	2.01	1.05	3.50	1.54	1.51
Expt. <sup>a</sup>	5.39	2.02	1.05	3.54	1.56	1.51

<sup>a</sup>Reference 18.

tently better than LDA calculations. It can be seen from Table I that both pseudopotentials obtain good results for all the low excited states. The HF pseudopotential, however, achieves better agreement with the experiments. Notice, too, that the HF pseudopotential always underestimates and the LDA always overestimates the binding energies. This is because the HF method neglects correlation, so the pseudopotential is slightly weaker than the pseudopotential generated from LDA calculations, which may have overestimated the correlation. This is consistent with the fact that HF calculations have obtained a larger lattice constant, while LDA calculations have obtained a smaller lattice constant. Interestingly, due to the cancellation of errors, our LDA calculation using the HF pseudopotential obtained the equilibrium lattice constant at 6.66 bohrs, in much better agreement with the experiment than results from HF calculations.

Our variational QMC calculations are based on the HF pseudopotential. LDA calculations are carried out for bcc Li using the first-principles pseudopotential total-energy approach.<sup>23</sup> Self-consistent single-particle wave functions are expanded using plane waves with kinetic energies up to 8 Ry. A  $(4 \times 4 \times 4)$  simulation cell containing 64 atoms is used for the calculation. The  $k$  points that satisfy periodic boundary conditions of the simulation cell and are occupied in LDA calculations are used to construct the Slater determinant.

The effect of the finite basis set is tested with LDA calculations. With a mesh of 512  $k$  points in the first Brillouin zone, the LDA total energy is lowered by 6.5 meV when the cutoff energy is increased from 8 to 12 Ry. The LDA total energy is further lowered by 1.5 meV when the cutoff energy is increased to 15 Ry. This level of convergence is due to the fact that the pseudopotential is much smoother than the Coulomb potential of lithium nucleus. We assume that the finite basis set has the similar effect on variational QMC results and conclude that a 8 Ry cutoff energy is adequate for this study.

Without the symmetric  $\Psi_j$  in Eq. (1), the HF calculations are carried out first. The initial 1000 steps per electron are used to reach equilibrium of the simulation configuration. An additional 10 000 steps per electron is used to evaluate the total energy. The per-step variation is fairly large at 0.6 eV with the average step size about 0.6 bohr. The results for a lattice constant at 6.60 bohrs are presented in Table II. Taking the difference between the HF total energy and the atomic ground-state energy (see Table I), we obtain a HF cohesive energy of  $0.61 \pm 0.03$  eV. All-electron HF calculations<sup>15</sup> have obtained 0.52 eV. Since there is no varia-

tional parameter for our HF calculations, the agreement serves to demonstrate that LDA wave functions are very similar to HF wave functions.

In order to determine the equilibrium lattice constant and bulk modulus, total-energy calculations are performed for lattice constant ranging from 6.2 to 7.2 bohrs. If the calculated energies are precise, the equilibrium lattice constant and bulk modulus can be simply obtained by a quadratic fit to the total energies. However, the energy obtained from QMC calculations can, at best, be treated as a random variable with a Gaussian distribution. To correctly treat this, many least-square quadratic fittings are carried out for QMC total energies that included Gaussian random variances. A statistical analysis of the fitting results gives not only the equilibrium lattice constant and the bulk modulus but also the statistical errors of these quantities. This process is equivalent to evaluating an average in  $M$ -dimensional space, with  $M$  being the number of lattice constants where total energies are calculated. Since  $M$  is usually small, use of the Metropolis algorithm<sup>20</sup> is not necessary. Results for the equilibrium lattice constant and bulk modulus are listed in Table III. Notice that a moderate statistical error for the HF total energy can produce large uncertainties for the lattice constant and bulk modulus.

With the Jastrow  $u$  term included in the trial wave function, the per-step variation reduces greatly to 0.2 eV. Because of the reduced per-step variation, well converged total energies are obtained with 4000 steps per electron in the simulation cell. For each chosen lattice constant, the parameter  $A$  is searched. In most cases, total energies at six to eight different values of  $A$  are calculated before the optimal value of  $A$  is determined. The optimal values of  $A$  are found to be within 15% of the uniform electron-gas value. We also have noticed that the total energy is not very sensitive to the value

TABLE II. Different energy terms at a lattice constant of 6.60 bohrs, for the  $(4 \times 4 \times 4)$  simulation cell. The units are eV and the statistical error in the last digits is in parentheses.

Term	HF ( $u=0$ )	QMC
kinetic energy	3.709(10)	4.124(15)
local potential	0.685(10)	0.698(10)
nonlocal potential	1.137(11)	1.134(11)
electron-electron	-3.981(32)	-5.231(12)
Ewald sum	-7.502	-7.502
total energy	-5.952(34)	-6.777(7)

TABLE III. Equilibrium lattice constant  $a_0$  in bohrs, bulk modulus  $B$  in kbar, and cohesive energy  $E_{\text{coh}}$  in eV. Numbers in parentheses are statistical errors estimated from the fitting procedure (see the text). The experimental values are for low temperatures and include zero-point energy.

Method	$a_0$	$B$	$E_{\text{coh}}$
HF	6.9(2)	140(60)	0.61(3)
QMC	6.72(1)	130(20)	1.57(1) <sup>a</sup>
Expt.	6.57 <sup>b</sup>	130 <sup>c</sup>	1.65

<sup>a</sup>Includes the finite-size correction from the  $(8 \times 8 \times 8)$  simulation cell.

<sup>b</sup>Reference 14.

<sup>c</sup>Reference 17.

of  $A$  within 10% of its optimal value. The results for lattice constant at 6.60 bohrs are listed in Table II together with the HF results. The optimal value of  $A$  at this lattice constant is 3.2, while the uniform electron-gas value is 3.4.

With the Jastrow  $u$  term, the charge density becomes smoother when compared to the HF charge density. The most significant change is a 10% reduction of the Fourier component  $(2\pi/a)(2,0,0)$  (and the equivalent directions). This is quite small when compared to other systems. In the case of silicon,<sup>9</sup> for example, the Jastrow  $u$  term changed the Fourier component  $(2\pi/a)(0,1,1)$  by a factor of 2 and, subsequently, the  $\chi$  term reduced the total energy by 1.8 eV per atom. From the small effect of the  $u$  term in the current case, we expect little energy gains from the use of the  $\chi$  term. For a lattice constant at 6.60 bohrs, we searched for the  $\alpha$  parameter [see Eq. (5)] between 0.0 and 2.0 and found no discernible energy reduction beyond the numerical noise. This is similar to what was found in the study of a high-density hydrogen crystal,<sup>24</sup> where it was also found that the use of the  $\chi$  term was unnecessary.

Calculations at other lattice constants are performed with only the Jastrow  $u$  term. The total energies are plotted in Fig. 1. The curve in Fig. 1 represents a least-squares quadratic fit to the energies. It is shown in Table III that the equilibrium lattice constant from variational QMC calculations is  $6.72 \pm 0.01$  bohrs, and the bulk modulus is  $130 \pm 20$  kbar. As discussed earlier, the equilibrium lattice constant and the

bulk modulus are obtained with consideration of random variances in the calculated total energies.

Finally, we address the issue of finite-size correction. Since periodic boundary conditions are employed and the Ewald method is used for the  $1/r$  potentials, the size correction is expected to be a uniform energy shift, so both the equilibrium lattice constant and the bulk modulus would not be affected. The total energy of the 64-atom simulation cell, from the minimum of the quadratic fit (see Fig. 1), is  $-6.78$  eV. That leads to a cohesive energy of 1.44 eV, or 0.21 eV smaller than the experiment. As a first step, the finite-size correction can be estimated from LDA calculations, as was done in earlier studies.<sup>9</sup> The LDA total energy of a 216-atom cell with a lattice constant at 6.6 bohrs showed a 0.11 eV reduction, while the total energy of a 512-atom cell showed a 0.15 eV reduction as compared to a 64-atom cell. The fully converged LDA calculation on an 8000-atom cell resulted in an energy reduction of 0.16 eV. With the LDA finite-size correction, the cohesive energy from variational QMC calculations becomes 1.60 eV.

To be certain of the finite-size correction, we have also performed variational QMC calculations on a 216-atom  $(6 \times 6 \times 6)$  and a 512-atom  $(8 \times 8 \times 8)$  cell with a lattice constant at 6.6 bohrs. Using the same  $A$  parameter as determined from the 64-atom cell calculations and 2000 steps per electron Monte Carlo walk, we have found an energy gain of 0.09 eV for the 216-atom cell relative to the 64-atom cell at the same lattice constant. Calculations on the 512-atom cell with 500 steps per electron walk showed a 0.13 eV energy gain. The similar finite-size effect obtained from the LDA and variational QMC calculations indicates that the finite-size correction beyond the 64-atom cell is mainly due to the sampling of the Fermi surface. It also shows that the correlation effect beyond 13.0 bohrs (average radius of a 64-atom cell) is about 0.02 eV. In comparison, a study on the correlation energy of bcc Li (Ref. 15) has estimated that the correlation energy beyond the third nearest neighbor (about 9.3 bohrs) is 0.11 eV. The finite-size correction for the 512-atom cell is probably negligible. Thus our variational QMC calculations have yielded 1.57 eV as the cohesive energy. This is within 0.08 eV of the experimental value. Even with the consideration of zero-point energy,<sup>25</sup> our cohesive energy is only 0.11 eV smaller than the experiment.

As Table III shows, the agreement between our variational QMC results and the experimental values is very good. The equilibrium lattice constant is still 2% larger. We believe that is the error introduced by the HF pseudopotential. In addition, our results show that a correlation indeed reduces the equilibrium lattice constant towards the experimental value. The bulk modulus has a large uncertainty that is mainly caused by the sensitivity of the second-order derivative. Calculations on more lattice constants will be effective in reducing the uncertainty of the bulk modulus. The numerical uncertainty of the cohesive energy is on the order of 5 meV. But it is difficult to estimate the error due to the pseudopotential. The atomic tests show that the error is less than 0.05 eV (see Table I). Since the error due to the pseudopotential will affect both the atom and solid, we expect only a fraction of 0.05 eV will show up as error in the cohesive energy. Based on this, we estimate that the uncertainty of

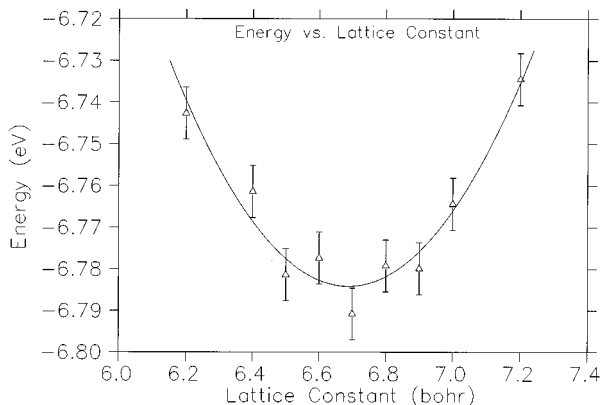


FIG. 1. Total energy vs lattice constant. The solid line represents a fit through the triangles.

cohesive energy is 0.01 eV. Unfortunately, 0.01 eV uncertainty may mask the energy difference between the bcc and the 9R structures.

Compared to all-electron variational QMC calculations,<sup>12</sup> the current approach clearly has advantages. The large fluctuation in energies is avoided and, as a result, we are able to achieve smaller variance with shorter simulation runs. The main advantage of the current scheme is a much better representation of the correlation for the conduction electrons. The parameter  $A$  is close to the uniform electron-gas result, as it should be. In the all-electron variational QMC calculations,<sup>12</sup> the very different correlation behavior of the  $1s$  core and the  $2s$  conduction electrons has forced the  $A$  parameter to a much smaller value of 0.4. We believe that this has led to a correlation for the conduction electrons that is much too weak to capture the major part of the correlation energy. The use of pseudopotential has enabled us to calculate accurate lattice properties and a cohesive energy with essentially one variational parameter.

The difference between the HF and the variational QMC total energy is the correlation energy. Our result (see Table II) is 0.83 eV. Obviously, this cannot be directly compared to the total correlation energy of 2.31 eV. However, if one assumes that the correlation associated with the  $1s$  core electrons is the same in the bulk as in the Li atom, one could subtract the correlation energy for the Li atom, 1.24 eV, from the total correlation energy. The result of 1.06 eV can be regarded as the correlation energy between the conduction electrons of bcc Li, which is close to our result of 0.83 eV. The correlation energy for the conduction electrons of bcc Li has been calculated using a local ansatz.<sup>15</sup> There the calculated correlation energy was 0.6 eV; the addition of an esti-

mated 0.3 eV due to the finite basis and another 0.1 eV due to the finite size gave the final correlation energy of 1.0 eV, in reasonable agreement with our variational QMC result.

The results show that the correlation energy between conduction electrons accounts for one-half of the total cohesive energy for bcc Li. In comparison, diamond has a cohesive energy of 7.4 eV and the correlation energy for valence electrons is 4.0 eV.<sup>9</sup> If we consider 2.0 eV as the intra-atomic correlation (the correlation energy among valence electrons in a carbon atom is 2.3 eV), then the interatomic correlation energy for diamond is only 27% of the cohesive energy, or 0.5 eV per valence electron. Calculations of the correlation strength<sup>15</sup> have also shown that bcc Li is one of the most strongly correlated system among all the  $sp$  simple systems.

In conclusion, we have performed variational QMC calculations for bcc Li using the pseudopotential generated from HF atomic calculations. The cohesive energy of 1.57 eV is, to the best of our knowledge, the most accurate QMC result reported. We want to point out that within the framework of pseudopotential the calculated Li atomic energy is exact, so the cohesive energy of Li crystal is bounded by the variational principle. The accuracy of the cohesive energy and other lattice properties is hence a good indication that our many-body wave function is close to the true ground-state wave function. Other physical properties such as the Compton profile, pair-correlation function, and correlation strength can be evaluated using this many-body wave function. Also we want to emphasize that the use of the pseudopotential, besides being computationally efficient in reducing numerical noise, can isolate the interesting interactions among the valence electrons and help us to gain insightful understandings of many interesting systems.

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