REGULAR ARTICLE

Variational grand-canonical electronic structure of Li+Li at ~10^4 K with second-order perturbation theory corrections

Shlomit Jacobi · Roi Baer

Abstract An ab initio variational grand-canonical electronic structure mean-field method, based on the Gibbs–Peierls–Bogoliubov minimum principle for the Gibbs free energy, is applied to the di-lithium (Li+Li) system at temperatures around $T \approx 10^4$ K and electronic chemical potential of $\mu \approx -0.1E_h$. The method is an extension of the Hartree–Fock approach to finite temperatures. We first study the Li$_2$ molecule at a frozen inter-nuclear distance of $R = 3$ Å as a function of temperature. The mean-field electronic structure changes smoothly as temperature increases, up to 10^4 K, where a sharp spontaneous spin-polarization emerges as the variational mean-field solution. Further increase in the temperature extinguishes this polarization. We analyze the mean-field behavior using a correlated single-site Hubbard model and show it arises from an attempt of the mean-field to mimic the polarization of the spin–spin correlation function of the exact solution. Next, we keep constant the temperature at 10^4 K and examine the electronic structure as a function of inter-nuclear distance R. At $R = 3.7$ Å, a crossing between two free energy states occurs: One state is "spin-unpolarized" (becomes lower in energy when $R > 3.7$ Å), while the other is "spin polarized". This crossing causes near-discontinuous jumps in calculated properties of the system and is associated with using the noninteracting electron character of our mean-field approach. Such problems will likely plague FT-DFT calculations as well. We use second-order perturbation theory (PT2) to study effects of electron correlation on the potential of mean force between the two colliding Li atoms. We find that PT2 correlation free energy at $\sim 10^4$ K is larger than at 0 K and tends to restore the spin-polarized state as the lowest free energy solution.

1 Introduction

The theoretical description of the detailed electronic structure of atomic gas plasma at high temperatures is of interest in strong laser interaction with matter, nuclear and shock-wave physics, astrophysics, and liquid metals [1–10]. Systems such as these involve mixtures of molecules and atoms in various charge states undergoing repeated collisions. For high-density plasma, one needs to use on-the-fly ab initio dynamics. Because of the complexity of such calculations, this can only be done in the context of finite temperature (FT) density functional theory (DFT) [11] using local/semi local exchange–correlation potentials "borrowed" from ground state DFT [6, 9, 10, 12–14]. The problem with this approach is that truly grand-canonical exchange–correlation density functionals are not available at present while use of ground state DFT is questionable [15].

For low-density plasma, one can simplify the problem considerably and use molecular dynamics based on a binary two-body potential of mean force obtained from electronic thermal ensemble calculations. This latter approach furnishes the motivation of the present study using as a specific example the Li+Li system. We do not use FT-DFT but instead resort to a grand-canonical variational method [16]. This approach is the natural extension of the Hartree–Fock theory for the grand-canonical ensemble and

S. Jacobi · R. Baer (✉)
Fritz Haber Center for Molecular Dynamics,
Institute of Chemistry, The Hebrew University
of Jerusalem, 91904 Jerusalem, Israel
e-mail: roi.baer@huji.ac.il

formally, the two theories become identical in the zero-temperature limit.

We study here several questions concerning treatment of electronic structure at high temperatures. For example, do we really need the variational approach or can we just use Hartree–Fock orbitals and orbital energies for the ensemble calculation? Another question is the importance of correlation effects: How important are they at medium temperatures? Finally, we would like to know what effects to expect in this mean-field theory. For example, mean-field theories often break symmetry in an attempt to mimic correlation effects; does this happen in the present system? What happens when we consider electron correlation beyond the mean field?

The application of this theory to the specific Li+Li system will enable us to address some of these issues, test potential pitfalls of the approach, and study the role of correlation energy using second-order perturbation theory. The structure of the paper is as follows: In Sect. 2, we review the variational approach; in Sect. 3, we will study the dependence of orbital energies as a function of temperature for a fixed inter-nuclear distance; Section 4 studies the free energy and the orbital energies as a function of temperature and inter-nuclear distance. In Section 5, we will discuss correlation free energy effects using second-order perturbation theory, and we finally summarize and discuss the results and conclusions in Sect. 6.

2 Background

We described the details concerning our implementation of the variational approach in Ref. [16], and we sketch out the essentials here. We consider the second-quantized Hamiltonian written as:

$$\hat{H} = t^t \hat{\rho} + \frac{1}{2} \hat{\rho}^T V \rho. \tag{1}$$

where the density matrix is

$$\hat{\rho}_{ij} = \sum_s \hat{c}_{si}^\dagger \hat{c}_{sj}. \tag{2}$$

Here, $\hat{c}_{si}^\dagger$ ($\hat{c}_{si}$) is the creation (destruction) operator of a spin s electron in orbital ψ_{is}. As shorthand notation, we define the composite index $I \equiv (ij)$ ($K \equiv (kl)$) and use the mathematical notation: $A^T B \equiv \Sigma_I A_I B_I$. The symmetric one-body t_I ($t_{ij} = t_{ji}$) and two-body V_{IK} ($V_{ijkl} = V_{klij} = V_{ijlk}$etc.) matrices are obtained as the integrals of the corresponding operators within the basis of the molecular orbitals and are defined in more detail in Ref. [16].

The Gibbs–Peierls–Bogoliubov variational principle [17–20] relates the Gibbs free energy $G_0 = -\beta^{-1} \ln Z_0$,

where $Z_0(\beta, \mu) = Tr\left[e^{-\beta(\hat{h} - \mu\hat{N})} \right]$, of a noninteracting electron system, with Hamiltonian $\hat{h} = h^T \hat{\rho}$, and the Gibbs free energy of the fully interacting electron system $G = -\beta^{-1} \ln Z$, with $Z(\beta, \mu) = Tr\left[e^{-\beta(\hat{H} - \mu\hat{N})} \right]$ as the following inequality:

$$G(\beta, \mu) \leq \Gamma(\beta, \mu) \equiv G_0(\beta, \mu) + \langle \hat{H} - \hat{h} \rangle_0. \tag{3}$$

Here, we define the grand-canonical averaging with respect to $\hat{h}$:

$$\langle \hat{O} \rangle_0 = \frac{1}{Z_0} Tr\left[e^{-\beta(\hat{h} - \mu\hat{N})} \hat{O} \right] \tag{4}$$

In these equations, the trace operations reference the space of all N-particle states ($N = 1, 2 \ldots$).

The right-hand side of the inequality in (3) is a functional $\Gamma[u]$ of the potential $u = h - t$, and one can minimize this functional to obtain the optimal potential u_* and the optimized approximation $\Gamma_*(\beta, \mu)$ to $G(\beta, \mu)$. The optimal potential u_* defines the optimal one-body effective single-particle Hamiltonian $\hat{h}_*$, spin-dependent eigenstates $\psi_{si}(\boldsymbol{r})$ and eigenvalues ϵ_{si} playing an analogous role to those of HF theory. The density matrix of the system depicts each orbital ψ_{si} as partially occupied according to its energy ϵ_{si} with the Fermi–Dirac weights $f_{si} = \frac{1}{1 + e^{\beta(\epsilon_{si} - \mu)}}$.

One can compare $\Gamma_*(\beta, \mu)$ with the HF free energy, based on the HF Hamiltonian $\hat{h}_{HF} = h_{HF}^T \hat{\rho}$:

$$\Gamma_{HF}(\beta, \mu) \equiv G_{HF}(\beta, \mu) + \langle \hat{H} - \hat{h}_{HF} \rangle_{\hat{h}_{HF}}. \tag{5}$$

where $\langle \hat{O} \rangle_{\hat{h}_{HF}}$ is the grand-canonical average with respect to $\hat{h}_{HF}$. We will study such a comparison below for the case where the chemical potential obeys the zero-temperature neutral system condition, namely: $-IP < \mu < -EA$, where IP is the ionization potential (approximated in HF theory by the highest occupied molecular orbital energy $-\epsilon_H$) and EA is the electron affinity (approximated by the lowest unoccupied molecular orbital energy $-\epsilon_L$). $\Gamma_{HF}(\beta, \mu)$ should be a reasonable approximation to $\Gamma_*(\beta, \mu)$ at low temperatures ($k_B T < \epsilon_L - \epsilon_H$). However, as temperatures grow, a full variational solution should become important.

3 Detailed temperature-dependent electronic structure at R = 3 Å

In this section, we single out an inter-nuclei distance, namely $R = 3$ Å, which is close to the HF bond length of Li_2, and study the predicted electronic structure as a function of temperature. This serves as a case study for studying the properties of the variational approach and for demonstrating that the minimization of Γ with respect to u,
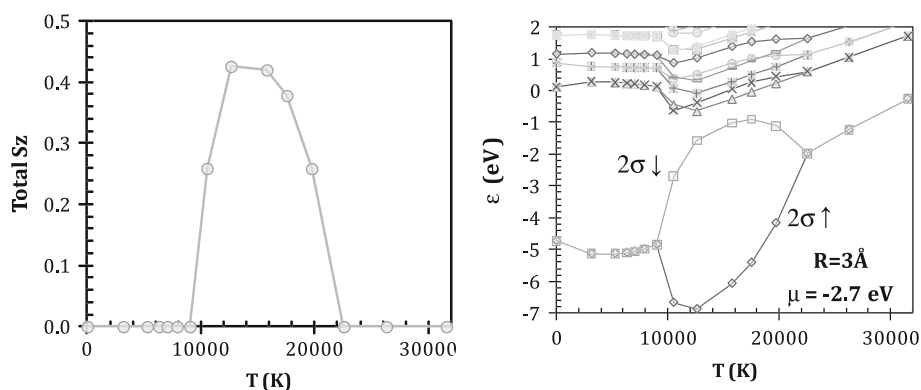
Fig. 1 *Left* the average z-component of spin on the Li+Li system as a function of temperature. *Right* the orbital energies of the variationally determined effective Hamiltonian $\hat{h}$ as a function of temperature for chemical potential $\mu = -2.7$ eV at Li−Li inter-nuclear distance of $R = 3$ Å. At low temperature, the valence $2\sigma\uparrow$ and $2\sigma\downarrow$ energies are degenerate. Once T exceeds 11,000 K these energies split, and become degenerate again when $T > 22,000$ K

instead of, for example, using the HF potential u_{HF}, is essential.

Figure 1 shows the spin orbital energies and the total spin component in the z direction of the system as a function of temperature. At the temperature range considered here, the 1σ and $1\sigma^*$ core orbitals are relatively unperturbed and remain fully populated. Naturally, the most important orbitals in this temperature range are the valence 2σ spin orbitals. Our approach is "open-shell", not forcing $\left(2\sigma_\uparrow\right)$ and $\left(2\sigma_\downarrow\right)$ orbitals to be spatially equal. When the population of the $\uparrow$ spin orbital becomes different from that of the corresponding $\downarrow$ spin orbital, we say that "spontaneous spin-polarization" has occurred. In Fig. 1 one sees that at $R = 3$ Å spontaneous spin-polarization indeed sets in, quiet abruptly, once the temperature exceeds a critical value, namely $\sim 11,000$ K. The Fermi–Dirac distribution determines the orbital occupancy, so spin-polarization is a direct result of the spin-up spin-down orbital energy differences (right panel). For all temperatures, these orbitals are inversion images of each other, namely $\hat{i}\left(2\sigma_\uparrow\right) = \left(2\sigma_\downarrow\right)$ and $\hat{i}\left(2\sigma_\downarrow\right) = \left(2\sigma_\uparrow\right)$, where $\hat{i}$ is the inversion operator through the middle point on the line joining the two Li nuclei. At low temperatures, a stronger condition holds, namely that the two orbitals have identical structure and therefore they are invariant to inversion: $\hat{i}\left(2\sigma_\uparrow\right) = \left(2\sigma_\downarrow\right) = \left(2\sigma_\uparrow\right)$; at higher temperature, the first equality continues to hold but the second does not. Thus, the orbital population loss is more significant on one of the two nuclei: The temperature-induced hole partially localizes. The orbital energy of 2σ in the 0 K (Hartree–Fock) calculation is -5.1 eV close to $-I$, where $I = 5.2$ eV is the experimental ionization potential of Li_2 [21]. The unoccupied orbital energies in Hartree–Fock theory are known to deviate considerably from the experimental electron affinity [22] EA = 0.4 eV. The energy of these orbitals, however, decreases rapidly as temperature rises, and they

become partially populated. One can interpret this in two ways, either as appearance of molecular excitations, that is, creation of electron–hole pairs, or the mixing-in of cation and anion states. Because our density matrix is constrained to describe noninteracting electrons, we are unable to discern these two physically distinct states. The orbital energy of the lowest "unoccupied" orbital, becoming partially occupied at temperatures above 10,000 K, dips to -0.65 eV, which is close to $-$EA. This stabilization of the electron affinity levels, when needed, is a welcome property of the present mean-field approach and deserves further investigation in a separate study. As the temperature grows, however, the importance of the anionic contribution diminishes since the cationic (ionization) contribution grows.

We now consider the reasons of appearance and subsequent disappearance of spontaneous spin-polarization in the 2σ orbitals discussed above. Under the chemical potential, we chose, the 2σ orbitals are fully occupied at zero temperature and there is no spin-polarization. As temperature increases, the population of these orbitals drops, due to ionization and in intermediate temperatures, above 10,000 K, spontaneous "spin-polarization", that is, nonzero value of the expectation value of S_z, appears because of this ionization. Let us explain this qualitatively. Suppose the system has to release one electron. It can do so by emptying one of the spin orbitals, say $2\sigma\uparrow$ completely leaving the $2\sigma\downarrow$ fully occupied or by taking "half an electron" from each of these orbitals. The first choice, leading to spin-polarization, minimizes electron repulsion but the second maximizes entropy. At sufficiently high temperatures, entropy maximization always "wins"; but, at lower temperatures, electron repulsion may be strong enough, and spin-polarization occurs. A more detailed description of these considerations appears in Appendix 1, where we analyze a single-site Hubbard model and

demonstrate analytically that conditions exist (Eq. 18) for which the spin-unpolarized solution is unstable with respect to a spin-polarization breaking perturbation (described by the parameter $\Delta \neq 0$). In Fig. 2, we show a regime supporting spin-polarization in the Hubbard model. The left panel of the figure displays the orbital occupation predicted by the variational method, compared with the exact occupation, where there is no polarization. In the exact calculation, there is no explicit spin-polarization anywhere because of symmetry. Yet, it does exist, although not in orbital populations; the two-electron density matrix reveals spin-polarization as a superposition of two spin-polarized states. In other words, the system displays quantum fluctuations between the two spin-polarized states. To expose these fluctuations, we consider the cross-correlation function $C = \langle (n_\uparrow - \langle n_\uparrow \rangle)(n_\downarrow - \langle n_\downarrow \rangle) \rangle$. We plot this quantity against temperature for the exact (Eq. 14) and the variational (Eq. 15) cases. Note that the value of C is negative because of electron repulsion. Without spin-polarization ($\Delta = 0$), the variational result has $C = 0$ and it is only through spin-polarization ($\Delta \neq 0$) that a nonzero negative cross-correlation can be built (see Appendix 1 for a more comprehensive explanation). The spin-polarization

in the variational treatment yields a negative value for C which is, however, much smaller than the exact value. This is due, mainly, to the very large value of the on-site repulsion parameter namely $U = 1E_h$ (smaller values of U do not result in spin-polarization (for $\mu = -0.1E_h$)). The variational treatment deviates from the exact result as the two-electron interaction strength U increases. In the molecule Li_2, the on-site repulsion U is about $0.2E_h$ and the fact that this is sufficient to cause spin-polarization is due to the existence of additional orbitals (sites).

We return to the question posed in the beginning of this section: do we really need the variational procedure? Perhaps the procedure of plugging u_{HF} into Γ is accurate enough. We expect, that for low temperatures, up to around 10,000 K this is a reasonable approach. This is because the orbital occupations and energies of the full variational treatment seem to change little with temperature in this range. However, at temperatures higher than 10,000 K, the orbital energies change dramatically. Previously unoccupied orbital energies are lowered (obtaining negative values) and become rapidly occupied while spin-polarization sets in. In this temperature regime, it is essential to use the full variational procedure.

4 Mean forces and their potentials

In this section, we study the force exerted by one Li atom on the other Li atom as a function of their distance R. The free energy $\Gamma(T, \mu; R)$ acts as a potential of mean force for the given temperature T and chemical potential μ. In the previous section, we showed that strong temperature effects set in around $T = 11,000$ K. We therefore, as a first step, study the electronic structure, namely the orbital energies, as a function of R at this temperature as shown in
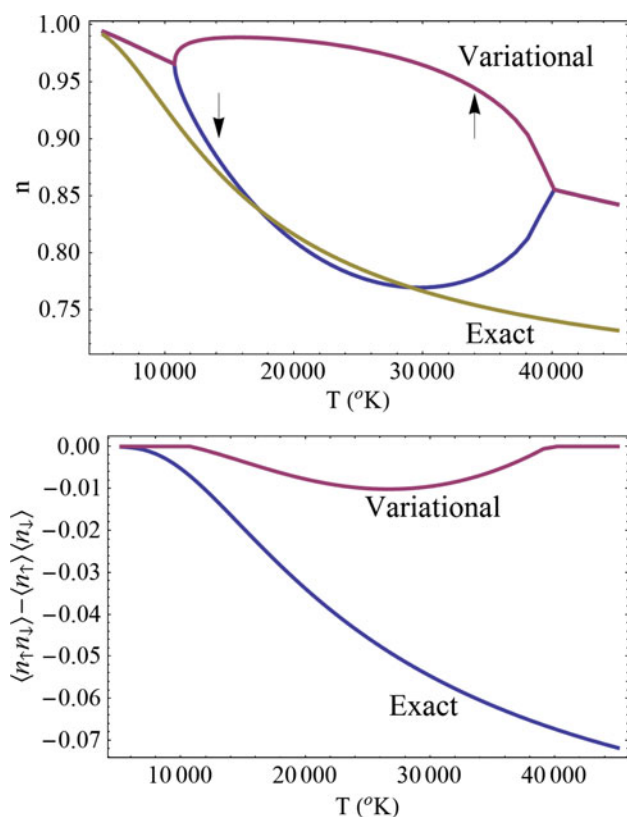

Fig. 2 Temperature-dependent spin-polarization in the single-site Hubbard model (with $U = 1.02E_h$, $h = -1.2E_h$, $\mu = -0.1$) variational approximation versus exact results: *Left* orbital populations ($n_\uparrow$ and $n_\downarrow$). *Right* The cross-correlation $C = \langle n_\uparrow n_\downarrow \rangle - \langle n_\uparrow \rangle \langle n_\downarrow \rangle$
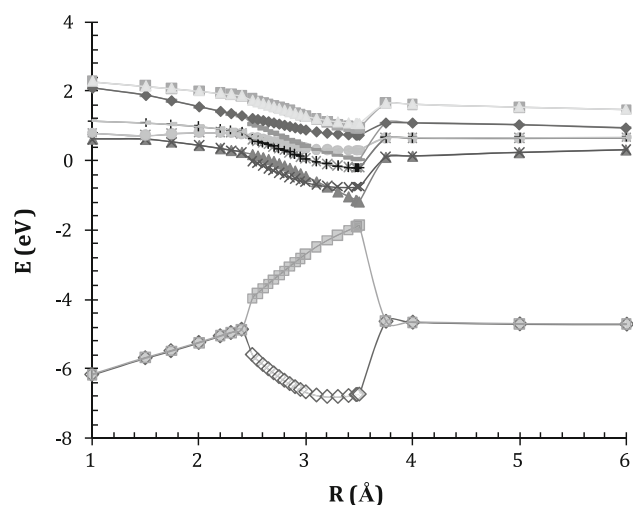

Fig. 3 The orbital energies as a function of Li−Li distance at $T = 11,000$ K

Fig. 3. It is evident that the spontaneous spin-polarization, discussed in the previous section for $R = 3$ Å, exists at lower and larger values of R as well. We see that, there is no spin-polarization at distances smaller than $R_c \approx 2.4$ Å. However, as R increases beyond R_c, the polarization grows significantly: One 2σ orbital is significantly stabilized and populated while the other is destabilized and depopulated. The system seems to be either losing an electron to the electron bath (ionization) at this regime or getting electronically excited (since the lowest unoccupied orbital energy decreases and becomes negative). Most likely, the density matrix is trying to describe a mixture of both processes. We notice a dramatic loss of spin-polarization at $R > 3.7$ Å. This effect is very sudden and in fact is a numerical artifact. What actually happens at this internuclear distance is orbital degeneracy. Thus, there are two fields here: u_1 responsible for breaking spin-polarization when $R > 3.7$ Å, yielding the minimal Γ, and u_2 giving a slightly larger value of Γ but preserving spin-polarization. We return to this issue below, when discussing electron correlation.

In Fig. 4 (top panel), we show the free energy, that is, potential of mean force, as a function of R for several temperatures. Comparing the potentials of mean force (top panel) for different temperatures, one sees that the shape is similar although the absolute value of the free energy decreases with temperature. Thus, it is better to compare their derivative, the curves of mean force (bottom panel). The curve of the lowest temperature considered (3,500 K) is very similar to that of zero temperature, and minimal energy is obtained at $R = 3.0$ Å, considerably larger than the experimental bond length of 2.6 Å. The depth of the HF potential (atomization energy) is 0.18 eV, which is an order of magnitude smaller than the experimental Li$_2$ atomization energy, of 1.1 eV. Clearly, the present approximation at low temperature, which is very close to the Hartree–Fock calculation, suffers considerably from lack of correlation energy. We will discuss correlation energy below.

For $T = 11,000$ K, we plot in Fig. 4 two curves, one corresponding to the lowest free energy, where spin-polarization is suddenly quenched and the other for the constrained spin-polarization case. The two curves, differ only slightly for $R > 3.5$ Å, despite their very different underlying electronic state origin.

The variational treatment predicts that the Li–Li potential has a basin of attraction at relatively large internuclear distances. However, the "bond length" (the internuclear separation minimizing the potential energy) is pushed to larger values as temperature increases. We shall see below that the attractive potential at $T > 10^4$ K disappears when allowing for electron correlation.
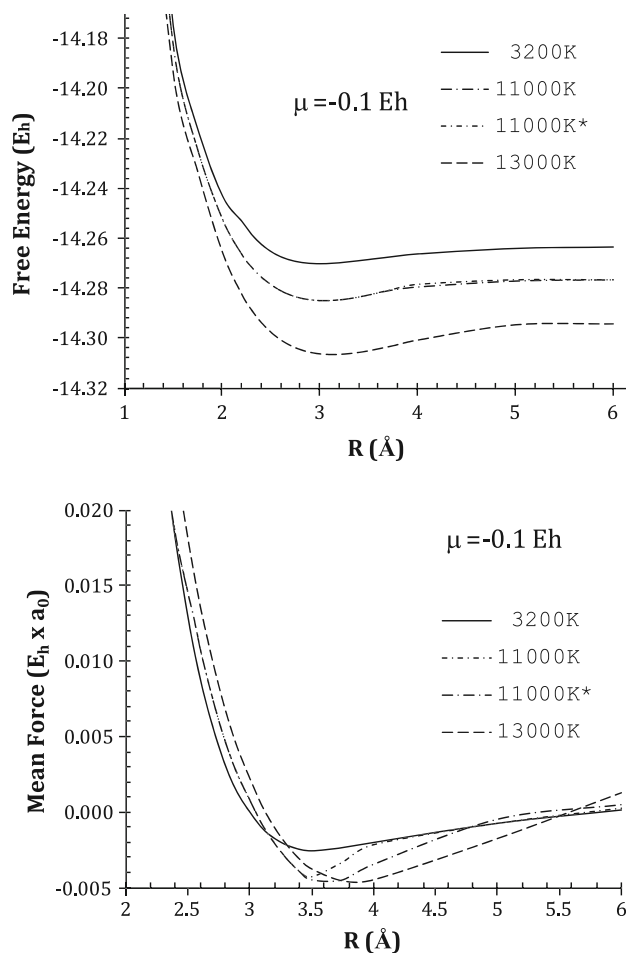

Fig. 4 *Top panel Curves* of potential of mean force for the Li–Li system at selected temperatures. At 11,000 K there are two nearly degenerate mean-field solutions. An *asterisk* depicts the higher energy curve. *Bottom panel* The mean forces derived from the potentials

5 Correlation effects using second-order perturbation theory

As discussed above, the variational approach lacks correlation energy. At zero temperature, the method is equivalent to the Hartree–Fock method and severely underestimates the binding energy of Li$_2$ (0.18e V vs. the experimental 1.1 eV); it also overestimates the bond length (3 Å vs. the experimental 2.6 Å). In order to take into account correlation, we use second-order perturbation theory (PT2) correction to the free energy, given by the following expression:

$$\delta G^{(2)} = -\frac{\beta}{4} \sum_{ijkl} f_i f_j \bar{f}_k \bar{f}_l h\big(\beta(\epsilon_i - \epsilon_l + \epsilon_j - \epsilon_l)\big) \big(V_{iljk} - V_{ijkl}\big)^2$$

(6)

where $f_i = \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}}$, $\bar{f}_i = 1 - f_i$, $h(y) = \frac{e^y - (1+y)}{y^2}$ and $h(0) = \frac{1}{2}$. In the zero temperature limit $(\beta \to \infty)$ $f_i(\bar{f}_j)$ is 1

(0) for HF occupied (unoccupied) spin orbitals. In this case, this expression reduces to the familiar Møller–Plesset perturbation theory [23].

At low temperatures, PT2 improves the HF bond length prediction from 3 to 2.7 Å very close to the experimental value of 2.6 Å. The potential-well depth predicted by PT2 theory is 0.45 eV, considerably deeper than that of HF theory (0.18 eV) but still too shallow relative to the experiment (1.1 eV). Moving to higher temperatures, we show in Fig. 5, the PT2 corrected potential of mean force at temperature of 11,000 K. Notice that the PT2 correction grows sharply with distance, showing that correlation effects become more significant as the atoms move away. The correction erases the small minima in the variational free energy curve resulting in a complete repulsive potential. As mentioned above, at $R \geq 3.7$ Å, there are two nearly degenerate mean-field solutions: u_1 that is not spin polarized and lower in free energy, and u_2 that preserves spin-polarization. One can see that by using the PT2-corrected free energy based on u_1 a discontinuous jump is obtained in the total curve when R crosses 3.7 Å. On the other hand, if we base the PT2 correction on the higher metastable free energy solution u_2, a smooth and more physically reasonable curve results. In addition, the total free energy is lower in this latter case, leading to the conclusion that this curve is the preferred estimate for the free energy. The fact that the two mean-field solutions are nearly identical in energy explains the unorthodox choice.

6 Summary and discussion

In this paper, we studied the electronic structure of the Li+Li system at temperatures of around 10,000 K and

chemical potential $\mu = -0.1 E_h$ as predicted by the variational approach to the grand-canonical free energy. We showed that orbital energies and their populations change rapidly with temperature; spontaneous spin-polarization occurs, explained using a simple single-site Hubbard model. Spin-polarization can occur in the model once the electron repulsion is strong enough and temperature is not too high (as Coulomb repulsion tends to polarize while entropy to depolarize). A similar phenomenon also occurs for the LiH system (see Fig. 6) at higher temperatures (16,000 K for inter-nuclear distance of 2 Å), because of the lower energy of the frontier orbitals.

We further studied the mean force and its potential between two Li atoms in the ensemble. The free energy correlation correction, estimated using second-order perturbation theory, is significant, especially at medium Li−Li distances, making the potential of mean force substantially more repulsive than estimated using mean-field theory alone. It is interesting to ask which of the exchange and correlation energies is dominant here. In ground state electronic, structure correlation energy is often smaller than exchange. However, here at 11,000 K, we see a case where the two energies are similar. The exchange energy is responsible for the spin-splitting of the orbital energies (actually, this split is caused mainly by that part of exchange that corrects the Hartree energy for self-interaction; thus calling this "exchange energy" may be misleading). The perturbative correction then restores the correct minimum by largely negating the effect of the exchange. From the correspondence principle, at high temperatures exchange energy eventually dies out as the system becomes more classical (spin-polarization also disappears). Correlation energy will still be there as mean field is not exact even in classical statistical mechanics.
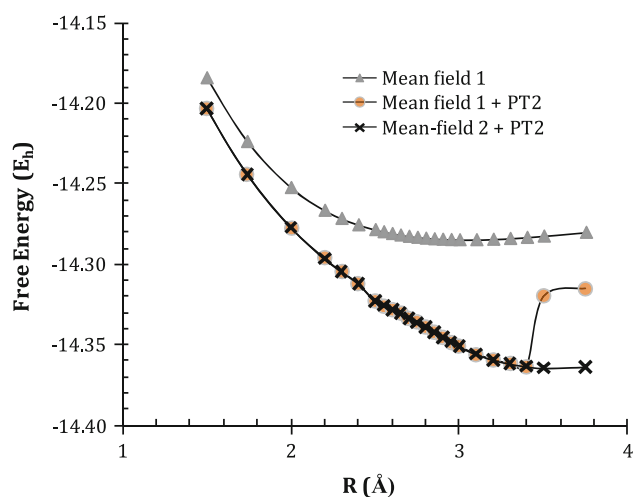

Fig. 5 The potential of mean force for the Li−Li system at 11,000 K: using the mean-field 1 (field that minimizes Γ), mean-field 1 + PT2 correction, and mean-field 2 + PT2 (mean-field 2 yields free energy slightly larger than that of mean-field 1, see Fig. 4)
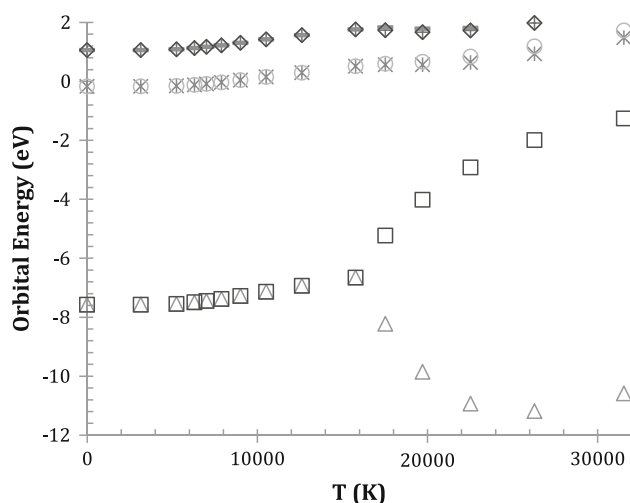

Fig. 6 The variational orbital energies as a function of temperature for the Li+H system at inter-nuclear separation of $R = 2$ Å

One can imagine that correlations might be introduced by the finite temperature Hartree–Fock–Bogoliubov (HFB) [24]. This method violates particle conservation but restores it on the average using a chemical potential, similar to the ensemble approach adopted here. However, for electrons, interacting via the purely repulsive Coulomb force, finite temperature HFB collapses to the present mean-field approach, giving nothing new (this is also true for ground state calculations) [25]. Perhaps a related but different approach to insert pair correlations, such as Scuseria's constrained pairing mean-field theory can be useful here [26, 27]. We leave this issue for future research.

Some of the conclusions inferred from this study are likely to impact future treatment of molecular systems at high temperatures. It seems that inclusion of correlation is of great importance, to no less degree than in zero-temperature calculations, at least for not too high temperatures. Moreover, the variational treatment encounters severe problems when frontier orbitals of different symmetry become degenerate and cross, causing discontinuities in the force of mean potential and orbital occupations. This complication results from the inherent noninteracting-electron nature of our variational mean field and is likely a general adverse feature of the approach: As temperature grows, the dense manifold of states representing the continuum becomes populated and orbital energy crossings are bound to occur.

One way, to insert correlation energy into this type of calculation is to use the FT-DFT approach [2, 3, 7, 9, 10, 12–14]. While this has the potential to improve performance with respect to correlation energy, [15] problems associated with frontier orbital-degeneracies, leading to multiple SCF solutions and discontinuities in observables, may still plague FT-DFT calculations as well.

Appendix 1

In this appendix, we construct a single-site model demonstrating spontaneous spin-symmetry breaking. If only a single site exists, there are four states: Site is empty; site has one electron, and there are two such options: Either a spin-up electron or a spin-down electron; and site has two electrons of opposite spins (Pauli's principle). The Hamiltonian of such a system is as follows:

$$\hat{H} = h(\hat{n}_\uparrow + \hat{n}_\downarrow) + U\hat{n}_\uparrow\hat{n}_\downarrow, \tag{7}$$

where h is the site energy, $\hat{n}_\uparrow$ and $\hat{n}_\downarrow$ are the number operators of $\uparrow$ and $\downarrow$ electrons, and $U > 0$ the repulsion energy between the two electrons occupying the site. At chemical potential μ and temperature $T = (k_B \beta)^{-1}$, the free energy is $G(\mu, \beta) = -\beta^{-1}\ln Z$ where the partition function is as follows:

$$Z(\beta, \mu) = 1 + 2x + e^{-\beta U}x^2 \tag{8}$$

where $x = e^{\beta(\mu-h)}$. The exact density matrix (DM) of the system is as follows:

$$\hat{\rho}_\downarrow = \frac{1}{Z}\left(\hat{\rho}_0 + x(\hat{\rho}_\uparrow + \hat{\rho}_\downarrow) + e^{-\beta U}x^2\hat{\rho}_{\uparrow\downarrow}\right). \tag{9}$$

Where, $\hat{\rho}_0$ is the DM of "no electrons" and

$$\hat{\rho}_\uparrow = \hat{a}_\uparrow^\dagger\hat{\rho}_0\hat{a}_\uparrow, \quad \hat{\rho}_\downarrow = \hat{a}_\downarrow^\dagger\hat{\rho}_0\hat{a}_\downarrow, \quad \hat{\rho}_{\uparrow\downarrow} = \hat{a}_\uparrow^\dagger\hat{a}_\downarrow^\dagger\hat{\rho}_0\hat{a}_\downarrow\hat{a}_\uparrow. \tag{10}$$

With $\hat{a}_\uparrow^\dagger \left(\hat{a}_\downarrow^\dagger\right)$ the creation operator for an electron in the spin-up (spin-down) site. The average up or down spin orbital occupation of the site is $\langle n_\uparrow\rangle = \langle n_\downarrow\rangle = \frac{x}{Z}\left(1 + xe^{-\beta U}\right)$ and the average double occupation is $\langle n_\uparrow n_\downarrow\rangle = \frac{xe^{-\beta U}}{Z}$.

Our variational approach locates the noninteracting system, with Hamiltonian $\hat{h} = h(\hat{n}_\uparrow + \hat{n}_\downarrow) + u_\uparrow\hat{n}_\uparrow + u_\downarrow\hat{n}_\downarrow$ and free energy $G_0 = \beta^{-1}\ln Z_0$, where $Z_0 = 1 + x\left(e^{-\beta u_\uparrow} + e^{-\beta u_\downarrow}\right) + x^2 e^{-\beta(u_\uparrow + u_\downarrow)}$, for which the functional $\Gamma = G_0 + U\langle n_\downarrow n_\uparrow\rangle - \left(u_\uparrow\langle n_\uparrow\rangle + u_\downarrow\langle n_\downarrow\rangle\right)$ is minimal and thus the closest approximation of its kind to G. The fields u_i $(i = \downarrow, \uparrow)$ are variational parameters that minimize this functional. It is more convenient to define $u_\uparrow = u + \Delta$ and $u_\downarrow = u - \Delta$ and $y = xe^{-\beta u}$. We write the partition function in terms of these quantities as:

$$Z_0(\beta, y, \Delta) = 1 + 2y\cosh\beta\Delta + y^2, \tag{11}$$

in addition, the orbital occupations are $\langle n_\uparrow\rangle_0 = \frac{y}{Z_0}\left(e^{-\beta\Delta} + y\right)$, $\langle n_\downarrow\rangle_0 = \frac{y}{Z_0}\left(e^{\beta\Delta} + y\right)$, finally, the joined occupation is $\langle n_\downarrow n_\uparrow\rangle_0 = \frac{y^2}{Z_0}$. Now, $\Gamma(U, \beta, x, u, \Delta)$ must be minimized with respect to u and Δ. If $\Delta \neq 0$, the DM is spin broken, and there are two variational solutions:

$$\hat{\sigma}_\pm = \frac{1}{Z_0}\left(\hat{\rho}_0 + y\left(e^{\mp\beta\Delta}\hat{\rho}_\uparrow + e^{\pm\beta\Delta}\hat{\rho}_\downarrow\right) + y^2\hat{\rho}_{\uparrow\downarrow}\right), \tag{12}$$

The numerical calculation singles out arbitrarily any one of these two solutions. One can also consider the "symmetrized" DM:

$$\begin{aligned}\hat{\sigma}_S &= \frac{1}{2}(\hat{\sigma}_+ + \hat{\sigma}_-) \\ &= \frac{1}{Z_0}\left(\hat{\rho}_0 + y\cosh\beta\Delta(\hat{\rho}_\uparrow + \hat{\rho}_\downarrow) + y^2\hat{\rho}_{\uparrow\downarrow}\right).\end{aligned} \tag{13}$$

While $\hat{\sigma}_S$ has the same partition function as $\sigma_\pm$, it has a larger free energy Γ. One way to describe spin-polarization in the system is by considering the cross-correlation function $C = \langle n_\uparrow n_\downarrow\rangle - \langle n_\uparrow\rangle\langle n_\downarrow\rangle$. In the exact treatment, this function is as follows:

$$C = -\frac{x^2}{Z^2}\left(1 - e^{-\beta U}\right). \tag{14}$$

For repelling particles ($U > 0$), the cross-correlation is negative, since repulsion reduces the probability of double occupation. In the variational treatment, using $\hat{\sigma}_{\uparrow\downarrow}$ leads to identically vanishing of the cross-correlation, namely $C_0 = 0$. However, under σ_S we have $\langle n_\uparrow n_\downarrow \rangle = y^2/Z_0$ and $\langle n_\uparrow \rangle = \langle n_\downarrow \rangle = (y^2 + y\cosh\beta\Delta)/Z_0$ so

$$C_0 = -\left(\frac{y\sinh\beta\Delta}{Z_0}\right)^2. \tag{15}$$

When $\Delta = 0$ the cross-correlation is zero but once spin-polarization occurs this cross-correlation becomes negative. Under this interpretation of the variational treatment, the spontaneous spin-polarization builds up as an attempt to mimic the underlying spin-polarization in the exact system.

We now examine the conditions under which spontaneous spin-polarization ($\Delta = 0$) can develop in the single-site model. Consider first a constrained variational treatment, namely setting $\Delta = 0$ and minimizing $\Gamma(U, \beta, x, u, \Delta)$ with respect to u only. The minimizing u, denoted u_* is then a solution of the following equation:

$$xe^{-\beta u_*}(U - u_*) = u_*. \tag{16}$$

Once β, U and x are given, this equation needs to be solved numerically for u_* and then $y_* = xe^{-\beta u_*}$. Next, we ask, what happens if we release the constraint $\Delta = 0$? We can test this by considering the derivatives of Γ with respect to Δ. Because of spin symmetry, the first order change $\partial\Gamma/\partial\Delta$ must be zero (since if Γ goes down when Δ is positive it must go up when it is negative, which is impossible because of spin symmetry). Therefore, we need to examine the second derivative:

$$\left.\frac{\partial^2\Gamma}{\partial\Delta^2}\right|_{\Delta=0} = \frac{2(1 + y_* - \beta u_*)}{(1 + y_*)^3}, \tag{17}$$

when positive $\Delta = 0$ is a stable minimum, while when negative symmetry spontaneously breaks. Clearly, spin symmetry $\Delta = 0$ is unstable when:

$$1 + y_* < \beta u_*. \tag{18}$$

At high enough temperatures, the spin symmetric solution is always stable, because then the right-hand side vanishes. But, at lower temperatures, spin-polarization is plausible.

Surprisingly, it is not that easy to find a symmetry-breaking regime in the model. First, one needs to set up the system to ensure double occupancy of the site at 0 K. For a given chemical potential, say $\mu = -0.1E_h$ (as we took for the Li$_2$ molecule), we ensure this by taking the ionization energy $h + U$ smaller than μ. Next, one has to increase U so that e–e repulsion is important. Simultaneously, we must decrease h so that $U + h < \mu$ continues to hold. We find that spontaneous spin-polarization does not occur when $U < 1E_h$ (and so h is of the order of $-1E_h$ too). Only at around $U \approx 1E_h$ do we notice spin-polarization. These conditions are far from those in the Li$_2$ molecule (where h and U are typically a factor 5 smaller). Clearly, the molecule is not a single-site system and thus spin-polarization occurs at much smaller repulsion strengths. In Fig. 2, we show the spin-symmetry break under these conditions. The populations of the spin-up and spin-down change considerably. The spin-down population decreases and approaches that of the exact model while the spin-up population is much closer to 1. Clearly, the variational treatment exhibits reduced ionization relative to the exact result. The right panel of Fig. 2 shows the cross-correlation functions of the exact and variational models as a function of temperature. The exact cross-correlation increases (in absolute value) as temperature increases in the regime shown. The variational cross-correlation value is zero up to the spin-polarization transition, where it dips to negative values. At high temperatures, spin ceases to polarize and the cross-correlation function quickly drops to zero again.

References

1. Rozsnyai BF (1972) Phys Rev A 5:1137
2. Perrot F (1979) Phys Rev A 20:586
3. Dharma-wardana MWC, Perrot F (1982) Phys Rev A 26:2096
4. Chen FF (1984) Introduction to plasma physics and controlled fusion. Plenum Publishing Corporation, New York
5. Braun A, Korn G, Liu X, Du D, Squier J, Mourou G (1995) Opt Lett 20:73
6. Hanfland M, Syassen K, Christensen NE, Novikov DL (2000) Nature 408:174
7. Surh MP, Barbee TW, Yang LH (2001) Phys Rev Lett 86:5958
8. Gurnett DA, Bhattacharjee A (2005) Introduction to plasma physics: with space and laboratory applications. Cambridge University Press, Cambridge
9. Kietzmann A, Redmer R, Desjarlais MP, Mattsson TR (2008) Phys Rev Lett 101:070401
10. Root S, Magyar RJ, Carpenter JH, Hanson DL, Mattsson TR (2010) Phys Rev Lett 105:085501
11. Mermin ND (1965) Phys Rev 137:A1441
12. von Lilienfeld OA, Tuckerman ME (2006) J Chem Phys 125:154104
13. Shiratori K, Nobusada K (2008) J Phys Chem A 112:10681
14. Tavernelli I, Vuilleumier R, Sprik M (2002) Phys Rev Lett 88:213002
15. Pittalis S, Proetto CR, Floris A, Sanna A, Bersier C, Burke K, Gross EKU (2011) Phys Rev Lett 107:163001
16. Jacobi S, Baer R (2005) J Chem Phys 123:044112
17. Gibbs JW (1902) Elementary principles in statistical mechanics. Yale University Press, New Haven
18. Peierls R (1934) Phys Rev 54:918
19. Kvasnikov J (1956) Doklady Akademii Nauk SSSR 110:755

20. Huang K (1987) Statistical mechanics, 2nd edn. Wiley, New York
21. Wheeler SE, Schaefer HF (2005) J Chem Phys 122:204328
22. Dixon DA, Gole JL, Jordan KD (1977) J Chem Phys 66:567
23. McWeeny R (1992) Methods of molecular quantum mechanics, 2nd edn. Academic Press, London
24. Goodman AL (1981) Nucl Phys A 352:30
25. Bach V, Lieb E, Solovej J (1994) J Stat Phys 76:3
26. Scuseria GE, Tsuchimochi T (2009) J Chem Phys 131:164119
27. Tsuchimochi T, Scuseria GE, Savin A (2010) J Chem Phys 132:024111