Fluctuations and Bonding in Lithium Clusters

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Structures and bonding of the Li_8 and Li_{20} clusters are investigated with path integral simulations combined with electronic structure calculations. The zero-point motion of the nuclei leads to quantum fluctuations corresponding to about 100 K thermal excitations. This destroys the distinction between long and short bonds which is a characteristic feature of the optimized static structures, but does not induce a qualitative change in the cluster structures or their electronic properties. [S0031-9007(98)05559-8]

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The investigation of clusters composed of metal atoms is an example where experiment and theory have currently reached a similar level of sophistication which leads to a fruitful interplay [1–3]. In recent years it has become clear that thermal fluctuations do play an important role in determining the properties of such clusters. Here we may mention thermal plasmon broadening [4,5] and the effects of a finite electronic temperature [6]. With the advent of atomistic *ab initio* molecular dynamics [7] it has become possible to study thermal effects beyond jellium-type models [2], while preserving a similar accuracy as the static electronic structure calculations [3]. Again, it was found that thermal fluctuations of the nuclear skeleton have sizeable consequences at experimentally relevant temperatures [8].

Clusters made up of the "lightest metal" may be special due to the small mass of the lithium nuclei. It is well known that the properties of helium or hydrogen clusters are dominated by the quantum mechanics of the nuclei at low temperatures, which leads to such phenomena as quantum-liquid behavior [9,10], superfluidity [11], binary phase separation [12], and plasticity [13]. In the case of lithium, quantum effects were recognized to be crucial for the understanding of the solid [14], but very limited attention was given to its clusters [15,16] despite the fact that the potential energy surfaces are known to be flat and to possess many minima of similar energy [3]. This property manifests itself in the interesting dynamics found in classical *ab initio* simulations of Li_n clusters at finite temperatures [17–20].

Recently, Li_n clusters with $n = 20$, 40, and 92 atoms were investigated at 30–600 K using path integral Monte Carlo simulations to include the quantum nature of the nuclei in conjunction with a finite version of the one-component plasma (OCP) to take into account the electronic structure [21]. The essential conclusions of this treatment are that "zero-point motion and tunneling play a crucial role in the determination of the structural and thermodynamic properties" and that "the clusters are fluidlike at all temperatures" [21]. However, this is in stark contrast with static electronic structure calculations: It is generally found that the optical spectra of small lithium clusters with up to eight atoms can be understood in terms of well-defined static structures [22–24]. It should be mentioned that the temperature dependence of spectra down to the order of 10 K is now experimentally accessible for small alkali clusters [25].

We resolve this controversy by *ab initio* path integral simulations [26] in the canonical ensemble (see Ref. [27] for details). Electrons and nuclei are treated on a similar level of accuracy after invoking the Born-Oppenheimer approximation [13,28]; a related strategy was followed in Ref. [16]. The nuclei are treated as distinguishable quantum particles within Feynman's path integral formulation of quantum statistical mechanics, which leads to efficient numerical schemes [29]. The electrons are included by *concurrent* first principles electronic structure calculations. This combination allows for nuclear quantum dispersion and tunneling on the electronic ground state energy hypersurface without taking recourse to model potentials to describe the Li-Li interactions. In particular, we supplement the local density approximation of the Kohn-Sham density functional theory [30] with Becke's exchange gradient correction [31], represent the two core electrons by a pseudopotential [32] including nonlinear core corrections [33], and expand the valence orbitals in a 30 a.u. periodic cubic box using plane waves with a cutoff of 15 Ry. This method gives excellent results not only for the Li_n structures but, more importantly, for the crucial energy differences between various isomers of a given cluster [34].

In order to make contact with both the electronic structure calculations [22–24] using $n \leq 8$ and the OCP path integral simulations [21] with $n \geq 20$, we selected the two cluster sizes Li_8 and Li_{20}. Low-temperature simulations [35] using Nosé-Hoover chains [27] were performed at 10 K with classical and ^6Li quantum nuclei (using a Trotter number [29] of $P = 16$ and, as a convergence test, $P = 32$ for Li_{20}). In addition, we explored thermal fluctuations at 100 K. We generated about 30 000–50 000 configurations after careful equilibrations and checked the data for convergence.

Let us start the discussion by analyzing the Li-Li bond length distribution of Li_8 and Li_{20} in Fig. 1, obtained by starting the simulations from annealed minimum potential energy configurations. The Li_8 cluster is characterized by two well-separated prominent peaks stemming from the nearest and second-nearest neighbor pairs. In the classical low-temperature simulation (dashed line), an additional splitting of both peaks is clearly discernible. This is a signature of the presence of short (≈ 2.8 Å) and long (≈ 3.1 Å) bonds as previously noted from static structure optimizations [34]. The same is true for the Li_{20} cluster, except that the distribution is much more structured due to the presence of third-nearest neighbors. The situation changes *qualitatively* when quantum fluctuations are taken into account at 10 K (solid lines): The bond length alternation is destroyed. Thus, the pronounced fine structure of the peaks vanishes and one is left with the coarse structuring in terms of neighbor shells only. An identical conclusion is reached when analyzing other quantities such as angle distributions or the radial one-body density which are not shown here. In order to get a feeling for the influence of the quantum effects in terms of thermal excitations we heated up the classical clusters. After increasing the temperature by a factor of 10 we find that thermal fluctuations at about 100 K (circles) qualitatively mimic the low-temperature quantum fluctuations; as expected the "matching temperature" depends on the property.

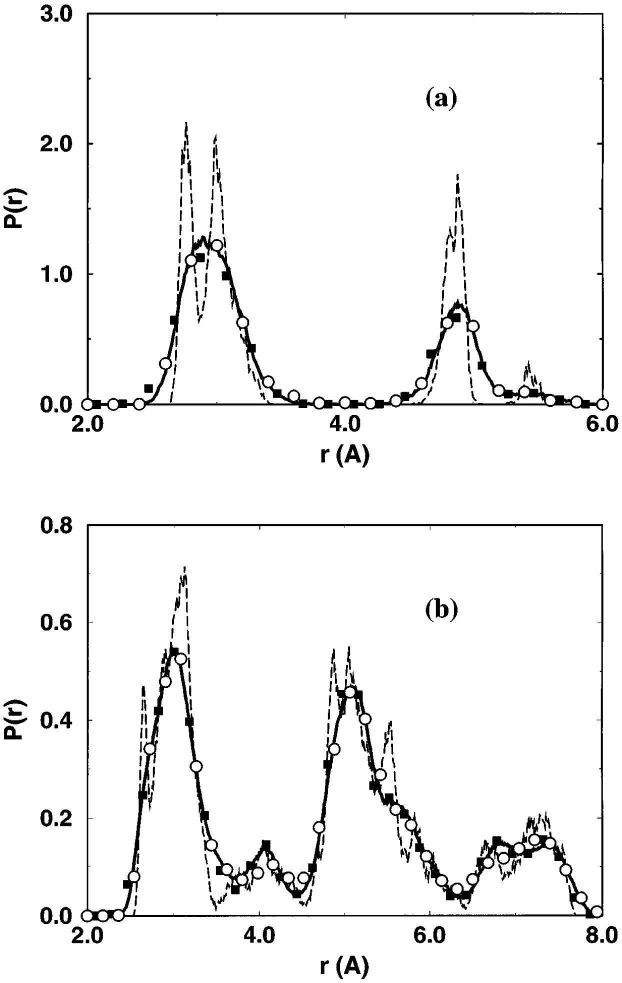

FIG. 1. Bond length distribution for Li_8 (a) and Li_{20} (b) clusters at 10 K with quantum (solid line) or classical (dashed line) nuclei, at 100 K with classical nuclei (circles), and at 10 K from a quasiharmonic broadening of the static optimized structures according to the text (squares); the integrals are normalized to unity.

An important thermodynamic measure to quantify the rigidity or floppiness of clusters is the rms relative bond length fluctuation [36],

$$\delta = \frac{2}{n(n-1)} \sum_{i<j} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle}, \tag{1}$$

where r_{ij} denotes the distance between the nuclei i and j. From our trajectories we find that δ is as small as 1% for the low-temperature classical simulations for both cluster sizes. This behavior is typical for frozen rigid structures. Quantum fluctuations at 10 K or classical fluctuations at 100 K lead to significantly larger values of about 4%–5% for both cluster sizes. However, this is still much lower than the value of typically $\delta \approx 10\%-20\%$ required to classify a cluster to behave liquidlike in the sense that it visits several distinct minima [36]. Thus, we clearly find that the cold quantum clusters are trapped around a minimum of the potential energy surface, but that the nuclei exert a non-negligible zero-point motion.

A shell-by-shell analysis of the amplitude of the zero-point motion is provided by the rms position displacement correlation function $R_i(\tau) = \langle |\mathbf{r}_i(0) - \mathbf{r}_i(\tau)|^2 \rangle^{1/2}$ in imaginary time $\tau \in [0, \hbar\beta]$, which measures the "size" $R_i(\hbar\beta/2)$ and, more importantly, the localization properties of a particle [37]; note that this quantity is strictly zero in the classical case. For Li_{20} we find that the innermost nuclei are most localized having a size of about 0.28 Å (compared to 0.78 Å for a free lithium nucleus at 10 K), but that the delocalization increases steadily to roughly 0.42 Å in the outermost shell. This latter value is identical to that obtained from the Li_8 cluster, where all atoms can be considered on the surface. Thus, we find that the most significant quantum fluctuations occur for the atoms on the *surface* of the clusters in qualitative agreement with the OCP model [21]. It is this zero-point motion of the order of a quarter to half an angstrom that ultimately destroys the distinction between the 2.8 and 3.1 Å short and long bonds which are a characteristic feature of static structures. On the other hand, we do not observe either tunneling or intershell particle exchange.

In the absence of tunneling it is tempting to explore how well a simple (quasi)harmonic approximation for the zero-point motion will fare. To this end, we compute the average nuclear radius of gyration [29]

$$\Delta = \left\langle \frac{1}{n} \sum_{i=1}^{n} \frac{1}{\hbar\beta} \int_0^{\hbar\beta} d\tau |\mathbf{r}_i(\tau) - \mathbf{r}_i^c|^2 \right\rangle^{1/2}, \tag{2}$$

which is another measure of a particle's size relative to its centroid, $\mathbf{r}_i^c = \int_0^{\hbar\beta} d\tau \mathbf{r}_i(\tau)/\hbar\beta$, and obtain $\Delta \approx$ 0.27 and 0.23 Å for the Li_8 and Li_{20} clusters at 10 K, respectively. *If* the quantum nuclei behaved like a collection of independent harmonic oscillators then one could emulate the quantum broadening of bond length distributions $P(r)$ at 10 K *exactly* by simply applying a Gaussian broadening $\propto \exp[-r^2/2\sigma^2]$ with $\sigma^2 = \Delta^2/3$ to the underlying optimized static structures that we started from. The essentially perfect agreement of these curves (squares) with the full quantum simulation at 10 K (solid lines) in Fig. 1 shows that (effective) harmonic zero-point motion can account for the observed quantum effects. At this stage, it is tempting to test an even rougher estimate based on the 351 cm^{-1} vibrational frequency of the Li_2 molecule [38]. However, this estimate provides a value of only $\Delta \approx 0.12$ Å which is not sufficient to destroy the bond alternation. Thus, the stiffer two-center bond found in the dimer cannot account for the most important aspects of the quantum fluctuations of lithium clusters.

Is it possible to understand the uncovered behavior in terms of the chemical bonding of the underlying static structures? This is achieved with the help of the electron localization function (ELF) [39]. This function $\eta(\mathbf{r})$ is large in regions where two electrons with antiparallel spin are paired in space, where its maxima can be associated with attractor basins due to electron pairing. ELF is normalized between zero and unity, and its value for the uniform electron gas is 1/2; note that our ELF analysis focuses exclusively on the chemically relevant valence electrons. In Fig. 2 we depict this function for Li_8 and Li_{20} as both an isosurface for $\eta^\star = 0.9$ to show all of the attractor basins and as a contour slice through the cluster centers to show the variation of ELF in space. This function reveals that there is a strong and anisotropic electron pair localization at the *surfaces* of both clusters, whereas pairing in the cluster core is of similar magnitude as in the homogeneous electron gas reference. This suggests the picture of localized surface states with directional bonding and a more metallic cluster core. It also explains the rigidity of the clusters with respect to major rearrangements since these are expected to occur mainly at the cluster surface via its intrinsic defects. It is this inhomogeneity and directionality of the chemical bonding which is underestimated by the uniform background of negative charge in the framework of the OCP model, where fluidlike behavior was found mainly on the cluster surfaces [21].

The ELF analysis in Fig. 2 furthermore reveals that the electron pairs associated with the basins are not shared among only two or three atoms each, but rather distributed over several atoms ("multicenter bonding") such that the number of face-sharing tetrahedral subunits is maximized. This picture of the structure and bonding relationship within these clusters is in line with the description of the structural building patterns found previously [40–43]. In addition, the present analysis shows that the long bonds are those that are contained within the basins of strong pairing, whereas the short bonds are preferentially located between such regions. Nevertheless, the topology of ELF does not change if the bond alternation of a particular isomer is distorted such that all bonds do have a similar length. Its topology, however, is in general clearly different for distinct isomers. This means that the observed quantum fluctuations do not induce a qualitative change of the electronic structure and thus of the associated excitation spectra relative to the underlying static isomer.

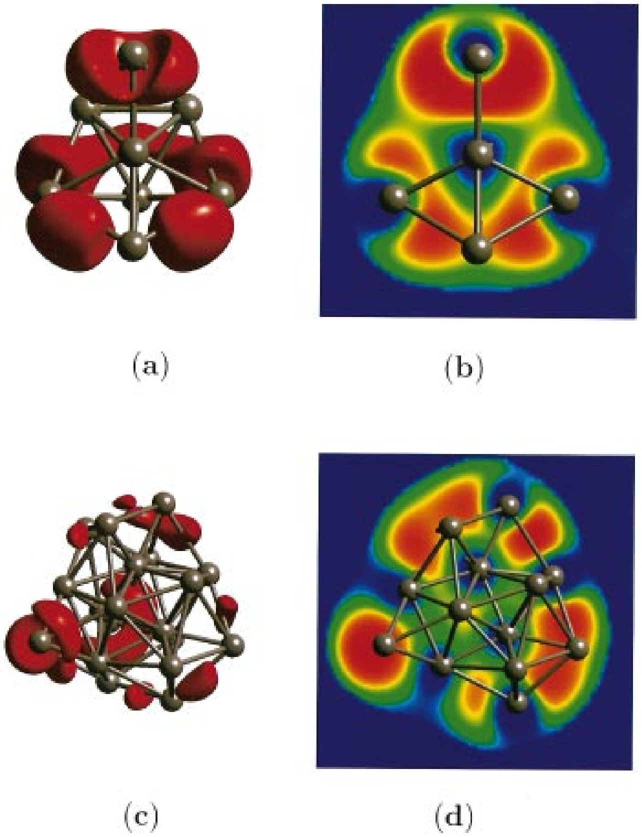

FIG. 2(color). Electron localization function $\eta(\mathbf{r})$ for the Li_8 (above) and Li_{20} (below) clusters. Left panels: isosurfaces for $\eta^\star = 0.9$. Right panels: contour slices through the cluster centers where red, green, and blue correspond to large ($\eta \gtrsim 0.9$), intermediate ($\eta \approx 0.5$), and low ($\eta \lesssim 0.2$) ELF values, respectively.

We also estimated the potential energy penalty associated with destroying one tetrahedral subunit, which is a crucial step in the rearrangement dynamics of isomers. This was done by studying energy differences between various isomers of Li_6 and Li_5^+, which provide a relative stability of one tetrahedral subunit of about 0.05–0.07 eV relative to reference structures with the less preferred three-center two-electron bonds. This value is similar to that obtained from the energy barrier of a representative isomerization reaction of Li_8. In this reaction a tetrahedral subunit is transmuted into a triangular arrangement on the surface, thus leading to a transition state. As monitored with ELF this reaction disrupts the regions of high-electron pairing by changing the topology of ELF and is associated with an activation barrier of 0.03 eV. Thus, we find that of the order of typically 0.05 eV are involved in such processes which surmounts the activation by zero-point motion as well as by thermal fluctuations at 100 K.

What is the overall picture that emerged from our analysis and its relevance to interpreting experiments? Taking properly into account both the electronic structure and the quantum motion of the nuclei, we reconcile the reported contradictory results. On the one hand, we confirm that quantum effects in small lithium clusters are indeed significant as they destroy the distinction between short and long chemical bonds, and effectively correspond to thermal excitations of about 100 K. On the other hand, the clusters are nevertheless quasirigid at low temperatures and the main consequence of the quantum fluctuations is a zero-point motion broadening of a single underlying structure. We do not find quantum-liquidlike behavior, neither tunneling nor particle exchange, between different shells. Thus, optical spectra of cold lithium clusters can be *qualitatively* understood with the help of electronic structure calculations of a few representative static species as a discriminative tool. However, *quantitative* agreement can be expected only if quantum dispersion is taken into account. An experimental confirmation of our findings would be temperature-independent spectra of cold clusters in the low-temperature limit.

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