Universal Shapes of Small Fermion Clusters

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Small atomic nuclei and clusters of alkali-metal atoms have similar shapes. We show that this similarity is a universal result of the density-functional theory. The shapes and the odd-even staggering of the total energy are nearly independent of the interactions between the fermions. [S0031-9007(97)02362-4]

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Physical models and quantum-chemical computations have shown that small clusters of alkali-metal atoms have shapes which are, in general, far from the most symmetric or nearly spherical geometry [1–7].

This is understood in terms of the Jahn-Teller effect [8]: a fermion system with a degenerate, partially occupied, highest molecular orbital (HOMO) spontaneously deforms in such a way that the degeneracy is lifted and a gap is opened at the HOMO level. Only clusters with electron numbers corresponding to shell closures (so-called magic numbers) can resist the Jahn-Teller effect. They then remain spherical and gain extra stability relative to clusters of neighboring electron numbers. The current theoretical understanding of cluster shapes is supported by experimental evidence provided by the photoabsorption spectra [9,10].

Similar shape deformations are present in small atomic nuclei. Nuclear shapes, however, have so far been mainly understood in terms of the internucleon forces [11]. In this Letter we wish to revise this view and propose that the deformation of small nuclei, too, is predominantly due to the Jahn-Teller mechanism [12]. According to our results, the shapes of small fermion clusters are universal and do not depend on the specific interparticle force. Insofar as shape is ascribed to shell structure [13,14], this means that shell structure is independent of the interparticle force.

Consider a system of identical fermions. Relevant realizations are the valence electrons in a cluster of alkali-metal atoms, the nucleons of a nucleus, or the atoms of ^{3}He liquid as an extreme example. Our purpose now is to show that the shapes of small clusters of these fermions in their ground state are universal. We use the density-functional Kohn-Sham theory (DFT) [15], where the total energy of the fermion system is written as a functional of the particle density $n(\mathbf{r})$:

$$E[n] = T_0[n] + V[n], \tag{1}$$

where $V[n]$ is the potential-energy functional of the true (interacting) system and $T_0[n]$ is the kinetic energy of independent fermions having the same density n as the true system. The density is calculated by means of auxiliary single-particle wave functions ψ_i as

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2. \tag{2}$$

Minimization of the energy functional (1) leads to the Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V_{\text{eff}}(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \tag{3}$$

where

$$V_{\text{eff}}(\mathbf{r}) = \frac{\delta V[n]}{\delta n(\mathbf{r})}. \tag{4}$$

A striking consequence of this formulation is that the full complexity of the nonlinear many-particle problem is now contained in the effective *single-particle* potential V_{eff}.

Since the exact energy functional is not known for any fermion system, the self-consistent set of equations can be solved only by using a suitable approximation for the potential-energy functional $V[n]$. However, it is important to realize that there *exists* an effective potential V_{eff} which gives the *exact* ground-state density.

The formal similarity of the treatment of all fermion systems can be emphasized by introducing a length parameter r_0 and writing Eqs. (3) and (4) in a dimensionless form:

$$-\tfrac{1}{2}\nabla^2_{\tilde{\mathbf{r}}}\phi_i(\tilde{\mathbf{r}}) + \tilde{V}_{\text{eff}}(\tilde{\mathbf{r}})\phi_i(\tilde{\mathbf{r}}) = \tilde{\epsilon}_i\phi_i(\tilde{\mathbf{r}}), \tag{5}$$

where

$$\tilde{\mathbf{r}} = \mathbf{r}/r_0, \quad \tilde{V}_{\text{eff}}(\tilde{\mathbf{r}}) = \frac{mr_0^2}{\hbar^2}V_{\text{eff}}(r_0\tilde{\mathbf{r}}), \quad \tilde{\epsilon}_i = \frac{mr_0^2}{\hbar^2}\epsilon_i. \tag{6}$$

For the density we now have

$$\tilde{n}(\tilde{\mathbf{r}}) = \sum_i |\phi_i(\tilde{\mathbf{r}})|^2. \tag{7}$$

It is natural to choose r_0 such that the equilibrium bulk density is the same for each fermion system. We choose r_0 so that the dimensionless density parameter (radius of the sphere containing one fermion) is $\tilde{r}_s = 4.18$, which is the value in atomic units for the electron gas [16]. This sets a common length scale and dimensionless kinetic energy for each fermion system in the bulk. It turns out that then also the dimensionless potential energy per particle is nearly the same in all the systems studied.

We now show that cluster shape is insensitive to the details of the effective potential. We use the local-density

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approximation (LDA) and write

$$\tilde{V}[\tilde{n}] = \int d^3\tilde{r}\,\tilde{n}(\tilde{\mathbf{r}})\tilde{v}[\tilde{n}(\tilde{\mathbf{r}})], \tag{8}$$

where $\tilde{v}$ is the potential energy per particle of the corresponding homogeneous system. We adopt the simple formula [17] $\tilde{v} = b\tilde{n} + c\tilde{n}^p$, where b, c, and p are parameters determined by the cohesive energy, bulk modulus, and density of the infinite system. With suitable parameters, this equation describes well the electron gas, nuclear matter, or liquid ^{3}He. The total (dimensionless) energy per particle in the homogeneous system is then $\tilde{e} = a\tilde{n}^{2/3} + \tilde{v}(\tilde{n})$, where the numerical value of the coefficient of the kinetic energy term is $a = (3/10) \times (3\pi^2)^{2/3}$. Figure 1 shows $\tilde{e}(\tilde{n})$ for the electron gas, nuclear matter, and ^{3}He.

With our adopted $\tilde{v}$ in Eq. (8), Eqs. (4) and (6) yield for the effective potential

$$\tilde{V}_{\text{eff}} = \partial(\tilde{n}\tilde{v})/\partial\tilde{n} = 2b\tilde{n} + (p+1)c\tilde{n}^p. \tag{9}$$

Equations (5), (7), and (9) now provide a well-defined problem for the density $\tilde{n}(\tilde{\mathbf{r}})$. It is solved iteratively by using a plane-wave basis and the fast Fourier transform [16].

We have calculated the density $\tilde{n}(\tilde{\mathbf{r}})$ for various sets of the parameters b, c, p, and for the number of particles (effective fermion number) $N = 2-22$ [18]. The resultant cluster shape is suitably characterized by multipole-expansion coefficients [16]

$$a_{lm} = \frac{4\pi}{3\tilde{r}_s^l N^{l/3+1}} \int d^3\tilde{r}\,\tilde{r}^l Y_{lm}(\theta,\phi)\tilde{n}(\tilde{\mathbf{r}}). \tag{10}$$

In our scheme the cluster is free to assume any shape; no symmetry restrictions are imposed.

Figure 2 shows representative results for the a_{lm} for clusters with $N = 6$ and 14. Surprisingly, the shape is seen to be nearly independent of the parameters of the energy function $\tilde{v}$, even though the (dimensionless) bulk modulus changes by a factor of 12 and the surface energy by a factor of 4 when going from the electron gas to ^{3}He. The same insensitivity of shape is true for small clusters of any N. Consequently, the intrinsic quadrupole moments of nuclei, which are proportional to a_{20}, can be calculated accurately with the density of nuclear matter as the only input parameter [19,20].

Comparison of shapes with those from the simple deformed shell models [13,14] can be made only qualitatively because our model allows *all* a_{lm} while the simple models are restricted to a_{20} as the only nonvanishing shape parameter. Nevertheless, our spheroidal shapes [16] are in substantial agreement with Clemenger [14].

Figure 3 (left) shows our calculated shapes for $N = 6$ and $N = 14$ clusters [21]. They are in perfect agreement with the shapes obtained with the Hartree-Fock method

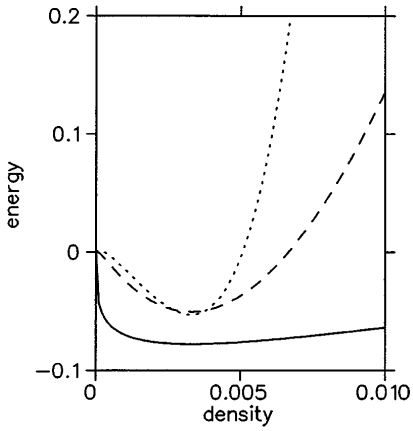

FIG. 1. Total energy per particle $\tilde{e}(\tilde{n})$ for electron gas (solid line), nuclear matter (dashed line), and ^{3}He liquid (dotted line).

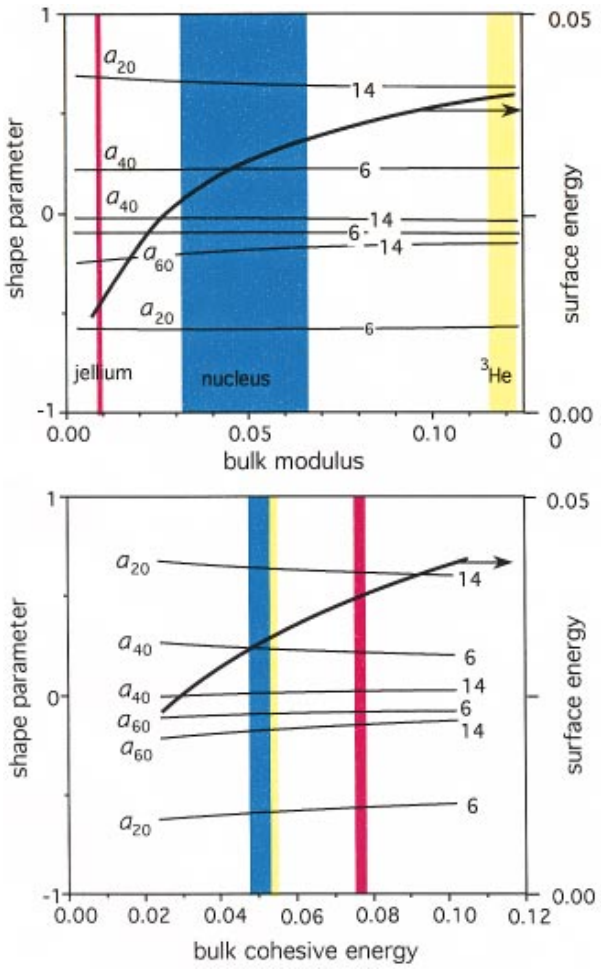

FIG. 2(color). Dependence of the shape parameters a_{lm} on the bulk modulus and cohesive energy for 6- and 14-particle clusters. Our cohesive energy and bulk modulus are defined as α and β in the expression $\tilde{\epsilon}(\tilde{n}) = -\alpha + \beta(\tilde{n}/\tilde{n}_0 - 1)^2$ for the energy per particle near equilibrium density $\tilde{n}_0$. The surface-energy parameter a_s is also given (thick solid line); it is defined by the mass formula $E = a_v N + a_s N^{2/3}$ (a_v is the volume-energy parameter). The regimes for the electron gas ("jellium"), nuclei, and ^{3}He are shown as colored areas. In the upper panel the cohesive energy and in the lower panel the bulk modulus are fixed to the value 0.05, respectively.

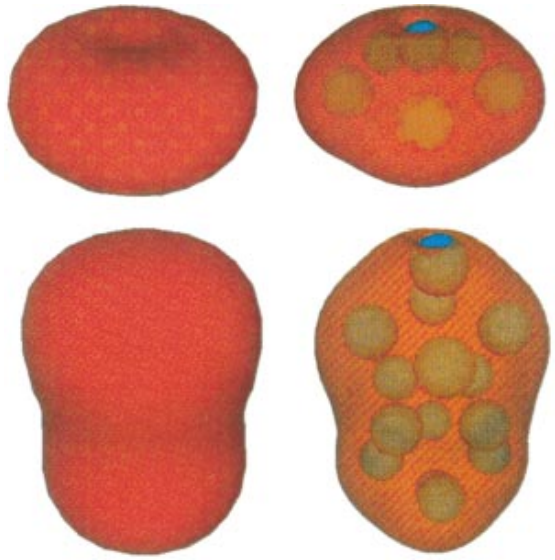

FIG. 3(color). Universal shapes of 6-particle (upper left) and 14-particle (lower left) clusters compared to geometries of Na_6 (upper right) and Na_{14} (lower right) calculated with DFT-LDA molecular-dynamics methods. In all cases the outer surface shown corresponds to the same particle density. Blue spheres represent the ions.

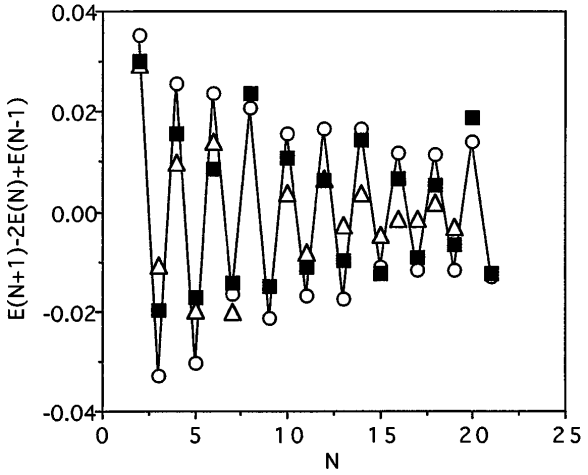

FIG. 4. Second derivative of the total energy as a function of the number of particles in the cluster. Black squares: unrestricted electron-gas model; open circles connected with solid line: experimental results for nuclei (with equal numbers N of neutrons and protons); triangles: experimental results for Na^+_{N+1} clusters.

for nuclei [22] and with a restricted electron-gas model [7]. For comparison we show (right) the ground-state geometries of the Na_6 and Na_{14} clusters we have calculated by DFT-LDA-based molecular-dynamics methods [23,24], where the interaction between valence electrons and discrete ions is described via pseudopotentials. The shapes defined by valence-electron densities are almost identical to those in the continuum model. The same geometry is in fact obtained regardless of the approximation used for the electron-ion many-body system (Hartree-Fock [3], configuration interaction [3], LDA [4], Hückel [25]).

The shape deformation reduces the wave-function symmetry to the twofold spin degeneracy, which leads to an odd-even staggering of the total energy versus particle number [26]. While the present local approximation fails to give correctly the total energy for any real system, it describes surprisingly well the odd-even staggering around the mean energy. Figure 4 shows the experimental data for nuclei [27] and Na clusters [28], scaled to the dimensionless form. They are compared with the results of the present model [16]. The near agreement suggests that, besides the shape deformation, also the odd-even staggering is a universal property of fermion systems. Especially, it is important to note that in the limit of small N the *experimental* odd-even staggering of Na clusters agrees with that measured for nuclei.

In nuclei the odd-even staggering is traditionally related to pairing of nucleons to Cooper pairs [29]. This cannot explain the similarity of Na clusters and nuclei. The binding energy of a Cooper pair in metals is about 10^{-5} in our dimensionless units, whereas it is about 10^{-2} in nuclear matter. Consequently the similarity of Na clusters and nuclei cannot be due to pairing of fermions to Cooper pairs. Rather the odd-even staggering in small nuclei appears to be a mere deformation effect as it is in Na clusters.

The insensitivity of the shape to the parameters of the local functional $\tilde{V}[\tilde{n}]$ and the agreement with the experimental results are strong indications that our results would not change even if nonlocal functionals, resulting from a proper treatment of the Coulomb field or gradient corrections, were used. For ^{3}He clusters, the gradient corrections are important because of the high surface energy present. The high surface energy in fact makes the smallest ^{3}He clusters unstable [30]. However, our calculations predict that once bound, ^{3}He clusters should exhibit shape deformations similar to those in other small fermion systems. While the surface energy would drive the cluster towards a more spherical shape [31], the resulting symmetric compression of nonspherical single-particle orbitals ($l > 0$) would simply cost too much energy due to the high bulk modulus of ^{3}He (see Figs. 1 and 2).

In conclusion, the density-functional Kohn-Sham theory provides a scheme which predicts a remarkably similar density profile and shape for any small cluster of N fermions, irrespective of the enormous differences in the fermion-fermion force. Our predictions agree with the available experimental evidence. The odd-even staggering of the total energy is intimately related to deformation and is similar in all fermion systems.

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