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Interaction between neutral sodium clusters: Short-range behavior

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The interaction potential between neutral magic sodium clusters (consisting of 2, 8, 20, and 40 atoms) is calculated within a two-center jellium model for the ionic cores. The results extend the long-range van der Waals potentials for these systems as determined by Pacheco and Ekardt [Phys. Rev. Lett. **68**, 3694 (1992)] to smaller cluster-cluster separations.

Interest in the interaction potential between clusters is motivated by a variety of problems, such as, for instance, the study of the formation and growth of atomic and molecular clusters,[1] the fusion and fission of clusters,[2–4] the embedding of clusters in bulk matter,[5] and the discussion of cluster-cluster collisions.[6] For a given cluster-cluster separation d (to be specified more precisely below) of two clusters X_N and Y_M the interaction potential U is defined as the difference between the ground state energy $E[X_N+Y_M](d)$ of the interacting two-cluster system and the corresponding energies $E[X_N, Y_M]$ of the isolated X_N and Y_M clusters,

$$U(d) = E[X_N + Y_M](d) - E[X_N] - E[Y_M] \quad . \qquad (1)$$

In a recent theoretical study Pacheco and Ekardt[7] (here referred to as PE) considered the (nonretarded) long-range limit of $U(d)$ for neutral magic sodium clusters on the basis of the spherical jellium model. They determined the leading two terms of the d^{-1} expansion of $U(d)$ for those d for which the density distributions of the two clusters do not overlap: This allows one to treat the cluster-cluster interaction perturbatively leading to the long-range van der Waals (vdW) potential $U_{\mathrm{vdW}}(d) = c_6/d^6 + c_8/d^8 + \cdots$, and its interpretation as a fluctuating dipole force.[8]

However, the condition of vanishing overlap and thus the regime of applicability of $U_{\mathrm{vdW}}(d)$ cannot be checked by a response calculation of the vdW coefficients. Thus the question arises at which separation a density overlap starts to build up and how $U(d)$ is modified in this regime, which is important for the discussion of the processes indicated above. It is this question which we try to answer in our contribution by a two-center calculation of $U(d)$ (which is necessarily required for this purpose) with the aim to establish a connection between those separations for which the clusters are in contact and the long-range vdW regime. Moreover, the interaction potential for those d which characterize the transition from two clusters X_N and X_M in contact to a united X_{N+M} cluster provides information on possible fusion and fission channels. In this respect, however, our present results can only serve as a starting point as a variety of geometrical aspects (like jellium neck formation) and the question of mass asymmetry have not yet been addressed.

We give results for the interaction potential between symmetrical pairs of neutral magic sodium clusters each containing 2, 8, 20, and 40 atoms,[9] obtained on the basis of a two-center jellium model[3] by fully self-consistent Kohn-Sham (KS) calculations. As is obvious from Eq. (1), $U(d)$ represents a ground state property of the two-center system such that in principle a two-center KS approach can reproduce the exact $U(d)$ obtained by solution of the corresponding two-center Schrödinger equation and thus in particular the correct long-range vdW behavior. However, all presently available approximations to the exchange-correlation energy functional do not contain the long-range correlation contributions responsible for the vdW attraction. This is, in particular, true for the local density approximation (LDA) which is used here such that we have to restrict ourselves to approaching the transition region to the vdW regime from small separations. This extends earlier studies[4] of cluster-cluster systems focusing on structural aspects of the Na_{19} dimer and the relation of the microscopic $U(d)$ to semiclassical concepts.

In the two-center jellium model each of the interacting clusters is characterized by a homogenous positively charged sphere of radius $R = r_S N^{\frac{1}{3}}$, where r_S denotes the Wigner-Seitz radius of the bulk metal ($r_S = 3.93$ a.u. for Na) and N is the number of atoms in the cluster. The cluster-cluster separation d is then given by the distance between the centers of the two spheres. The electrostatic potential $v_+(\boldsymbol{r})$ resulting from the jellium charge density $n_+(\boldsymbol{r})$ (for symmetric pairs),

$$\begin{aligned} n_+(\boldsymbol{r}) = n_0\, &[\Theta(R^2 - \rho^2 - (z - d/2)^2) \\ &+ \Theta(R^2 - \rho^2 - (z + d/2)^2)], \quad d \geq 2R \end{aligned} \qquad (2)$$

[in cylindrical coordinates, $n_0 = 3/(4\pi r_S^3)$ for alkali metals] binds the valence electrons. For cluster-cluster separations for which the two spheres overlap, $n_+(\boldsymbol{r})$ is kept homogenous and equal to n_0 inside the two-center system by adjusting the radius R_d of the overlapping spheres such that the total volume of the system is conserved,

$$n_+(\boldsymbol{r}) = n_0\, \Theta(R_d^2 - \rho^2 - (|z| - d/2)^2) \quad , \quad d < 2R \qquad (3)$$

$[8R^3 = R_d^2(4R_d + 3d) - d^3/4]$. For this axially symmetric two-center system we solve the KS equations (for a sufficiently fine grid of intercluster separations d),

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + v_+ + v_H + v_{\mathrm{xc}} \right) \Psi_\alpha = \epsilon_\alpha \Psi_\alpha \quad . \qquad (4)$$

Here v_H and v_{xc} denote the Hartree and the exchange-correlation potentials, respectively. For exchange and

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correlation we use the LDA in the form given by Vosko, Wilk, and Nusair.[10] Equation (4) is solved by basis expansion of the single-particle orbitals Ψ_α in terms of the Hylleraas functions

$$\psi_{nlm}(\xi,\eta) = (\xi^2-1)^{\frac{m}{2}} e^{-\frac{\xi-1}{2a}} L_n^m\left(\frac{\xi-1}{a}\right) P_l^m(\eta) \ , \quad (5)$$

using prolate spheroidal coordinates ξ, η, φ. In our calculations a set of 18 generalized Laguerre polynomials L_n^m and 20 associated Legendre functions P_l^m has been used. The parameter a is adjusted to reproduce the asymptotic behavior of the exact Ψ_α as accurately as possible (compare Ref. 4). With this basis set the absolute numerical errors of our two-center LDA (TC/LDA) results are smaller than 1 meV for $(\mathrm{Na}_2)_2$ and $(\mathrm{Na}_8)_2$ and of the order of 20 meV and 50 meV for the computationally more demanding $(\mathrm{Na}_{20})_2$ and $(\mathrm{Na}_{40})_2$, respectively (these errors can be estimated directly from the difference between the ground state energy obtained for a spherical Na_N cluster within a fully numerical one-center calculation and the $E[Na_N]$ found on the basis of the present two-center code with a spherical Na_N located at one of the centers).

The asymptotic behavior of the resulting $U_{\mathrm{TC/LDA}}(d)$ (and also the accuracy of our results) is demonstrated in Fig. 1 using $(\mathrm{Na}_8)_2$ as an example. As is well known[11,12] the LDA does not reproduce the correct d^{-6} behavior of $U(d)$ but rather leads to an exponentially decaying cluster-cluster potential due to the short-range nature of the LDA exchange-correlation potential [note that recently there have been several suggestions to overcome this deficiency of the LDA (Refs. 12 and 13)]. This exponential decay for large d is illustrated in Fig. 1 by comparing our numerical $U_{\mathrm{TC/LDA}}(d)$ with a simple exponential decay, $U_{\mathrm{fit}}(d) = U_0 e^{-\alpha d}$, whose parameters have been fitted to the numerical $U_{\mathrm{TC/LDA}}(d)$ at $d = 28$ a.u. and $d = 24$ a.u. However, the present work only addresses separations for which one finds density overlap such that short-range correlations dominate over fluctuation phenomena and thus this limitation of the LDA is irrelevant.

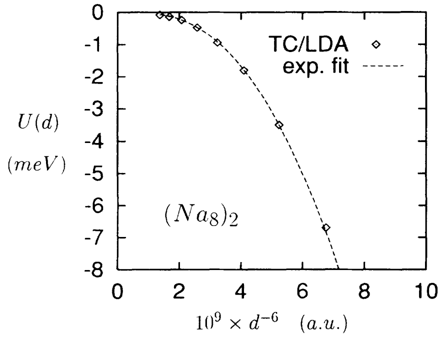

FIG. 1. Asymptotic form of $U_{\mathrm{TC/LDA}}(d)$ compared with an exponential fit as a function of d^{-6}. Note that for obtaining $U_{\mathrm{TC/LDA}}(d)$ for each d the two-center energy $E[(\mathrm{Na}_8)_2](d)$ and the single-cluster energy $E[\mathrm{Na}_8]$ have been calculated using the two-center code with identical basis sets, thus reducing the error in $U_{\mathrm{TC/LDA}}(d)$ due to basis set truncation by about one order of magnitude. The largest discrepancy between the $E[\mathrm{Na}_8]$ evaluated in this way and a fully numerical one-center calculation is 0.18 meV (for $d = 30$ a.u.).

Our results for $U_{\mathrm{TC/LDA}}(d)$ are given in Fig. 2 together with $U_{\mathrm{vdW}}(d)$ of PE. Also indicated in the figures are the separations at which the two spherical jellia come into contact, i.e., $d_c = 2R_{\mathrm{Na}_N}$. A comparison of

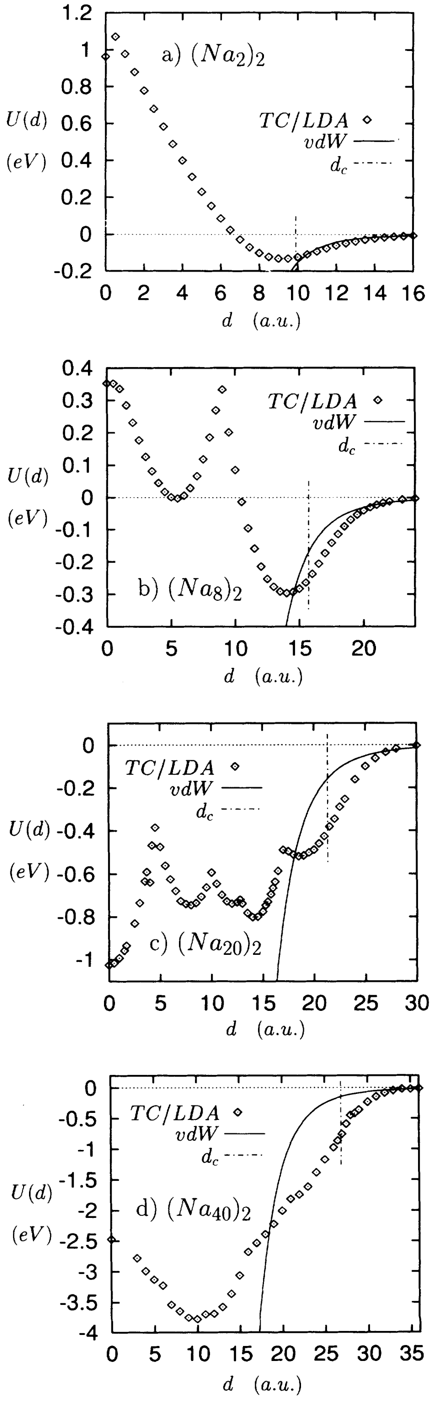

FIG. 2. $U_{\mathrm{TC/LDA}}(d)$ from Eq. (1) (TC/LDA) in comparison to $U_{\mathrm{vdW}}(d)$ from Ref. 7: (a) $(\mathrm{Na}_2)_2$; (b) $(\mathrm{Na}_8)_2$; (c) $(\mathrm{Na}_{20})_2$; (d) $(\mathrm{Na}_{40})_2$. The vertical line indicates the contact point d_c of the two Na_N clusters.

$U_{\mathrm{TC/LDA}}(d)$ with $U_{vdW}(d)$, of course, is only meaningful beyond the point of contact d_c. The corresponding valence electron densities along the symmetry axis of the systems are shown for three cluster-cluster separations in Fig. 3 (only the positive z regime is plotted). The values of d in Fig. 3 have been chosen to cover the separations for which the two-center systems develop from large to vanishing density overlap. In particular, the intermediate d values are roughly those cluster-cluster separations for which $U_{\mathrm{vdW}}(d)$ and $U_{\mathrm{TC/LDA}}(d)$ coincide. They thus represent lower bounds for the regimes in which $U_{\mathrm{vdW}}(d)$ can be expected to give realistic results. The other two separations shown bracket these values of d.

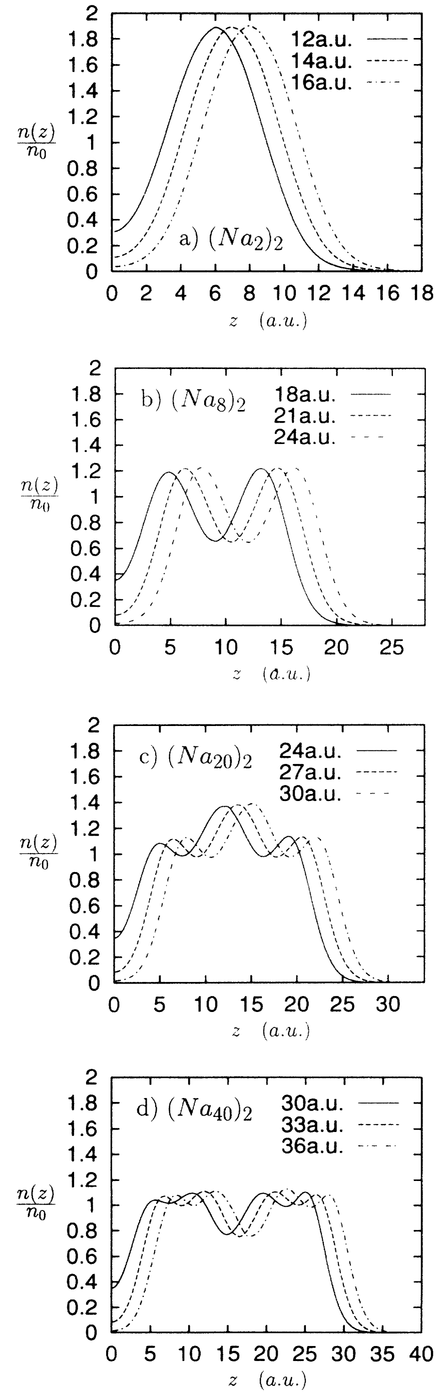

FIG. 3. Density profiles along the symmetry axis (normalized to the bulk value n_0) at different intercluster separations: (a) $(Na_2)_2$; (b) $(Na_8)_2$; (c) $(Na_{20})_2$; (d) $(Na_{40})_2$.

For $(Na_2)_2$ [Fig. 2(a)] $U_{\mathrm{TC/LDA}}(d)$ and $U_{\mathrm{vdW}}(d)$ are rather close together over the complete range of interest ($d > d_c$). Thus $U_{\mathrm{vdW}}(d)$ reproduces $U_{\mathrm{TC/LDA}}(d)$ fairly well even for d close to the contact separation d_c for which the electronic densities of the dimer components overlap substantially [compare Fig. 3(a)]. In view of the usual criterion for the validity of the vdW form this appears to be a somewhat unexpected behavior. This result must, however, be regarded as fortuitous: It is specific to the $(Na_2)_2$ system for which $U_{\mathrm{TC/LDA}}(d)$ is strongly repulsive for $d < d_c$. Moreover, all results based on the jellium model for systems as small as $(Na_2)_2$ should not be taken too seriously in view of the drastic deviation of the model geometry from the real structure of these clusters.[14]

For all larger systems, as expected, the picture changes considerably. For $(Na_8)_2$ [Fig. 2(b)] $U_{\mathrm{TC/LDA}}(d)$ is noticeably different from $U_{\mathrm{vdW}}(d)$ in the region close to contact ($d_c = 2R_{\mathrm{Na_8}} = 15.72$ a.u.). While at d_c the $U_{\mathrm{TC/LDA}}(d)$ is 50% more attractive than $U_{\mathrm{vdW}}(d)$, their difference decreases smoothly with increasing d, both potentials merging at about $d = 21$ a.u., which represents a surface-surface separation of 5 a.u. The same trend, but more pronounced, is found for $(Na_{20})_2$ and $(Na_{40})_2$. However, while the magnitude of the differences for $d \approx d_c$ increases with cluster size [for $(Na_{20})_2$ and $(Na_{40})_2$ $U_{\mathrm{TC/LDA}}(d_c)$ is a factor of 2.5 and 5, respectively, more attractive than $U_{\mathrm{vdW}}(d_c)$], the range of separations for which U_{vdW} is inappropriate is rather similar for all systems, extending from contact to surface-surface separations of about 5 a.u. We thus find that apart from the somewhat special $(Na_2)_2$ system the full $U(d)$ is always much more attractive for small intercluster separations, i.e., in a region which is relevant for the cluster reactivity in collisions and cluster formation and fusion processes. Moreover, while one would expect neither the TC/LDA results nor the vdW results to be very accurate in the transition regime around $d_c + 8$ a.u. and it is not clear at present whether the smooth match of $U_{\mathrm{TC/LDA}}(d)$ with $U_{\mathrm{vdW}}(d)$ for $d \approx d_c + 5$ a.u. must be regarded as fortuitious or not, this matching nevertheless suggests that a combination of $U_{\mathrm{TC/LDA}}(d)$ for values of d smaller than this matching separation and $U_{\mathrm{vdW}}(d)$ for larger d could be a realistic estimate of the complete $U(d)$.

The origin of the structure of $U_{\mathrm{TC/LDA}}(d)$ for overlapping jellium spheres has been discussed in detail in Ref. 4: Each peak reflects a new single-particle orbital entering the occupied spectrum, as can be seen from the KS eigenvalues as a function of d. Thus the rich structure for the Na_{20} dimer is due to a variety of level crossings at the Fermi surface during the adiabatic fusion process following the chosen geometry. In contrast, for the Na_{40} dimer most of this structure is washed out as a consequence of the reduced level spacings in this larger system. Furthermore, the pronounced minimum at $d \approx 10$ a.u. is an indication of a possible deformation of the compound cluster Na_{80}. Deformation effects can also be seen for $(Na_2)_2$ and

$(Na_8)_2$: Our results are consistent with the known large prolate deformation of Na_4 (within the jellium model[15]) and indicate that Na_{16} is also a deformed system, as a nonspherical jellium leads to a lower ground state energy than a spherical background. Of course, our dimer geometry does not represent the correct ground state geometry of Na_{16}, which shows oblate deformation.[15] In contrast to these systems, Na_{40} is spherical which is also obvious from Fig. 2(c).

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