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Metastability of doubly charged transition-metal dimers in density-functional theory

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We have performed pseudopotential density-functional-theory computations for four doubly charged dimers of the IB (Ag_2^{2+},Au_2^{2+}) and IIB (Cd_2^{2+}, Hg_2^{2+}) groups. Within the local-density approximation the potential-energy curve for Ag_2^{2+} is monotonically repulsive. The other three dimers, instead, are metastable, with a fission barrier Δ of 0.1 eV for Au_2^{2+}, 0.9 eV for Cd_2^{2+}, and 1.1 eV for Hg_2^{2+}. After inclusion of gradient corrections to the exchange and correlation functional, the fission barrier for gold vanishes. Those for cadmium ($\Delta=0.65$ eV) and mercury ($\Delta=0.7$ eV), although reduced, remain important and sufficient to ensure the detectability of these metastable dimers.

Recent experimental results[1] have revived the debate on the existence as metastable species of doubly charged transition-metal dimers.

Since its beginning, this subject has mainly been of interest to theoretical physicists and quantum chemists. In fact, given the delicate balance of repulsive and attractive forces, these systems provide a useful and sensitive gauge for theories. An early discussion of the bonding in Hg_2^{2+}, and of the role of relativistic effects in stabilizing this dimer, was reported in Ref. 2. A systematic analysis within semiempirical models of stability for doubly charged transition-metal dimers was carried out in Ref. 3. Several other results are reported in a number of papers.

To our knowledge, the only species experimentally observed in the gaseous phase are Mo_2^{2+} (Ref. 4) and Au_2^{2+}.[1] The experimental evidence for the last dimer, in particular, has been the focus of some controversy. On the one hand, extensive computations performed within the standard quantum-chemistry methods (configuration interactions,[5] Hartree-Fock[6]) predicted the Au_2^{2+} dimer to be unstable in the ground state. On the other hand, approximate computations within the density-functional framework[7] confirmed the observability of Au_2^{2+} as a metastable species, with a fission barrier of 0.8 eV. Finally, semiempirical models were able to interpolate between the two theoretical limits.[8,9]

In the present paper we report pseudopotential-density-functional computation of the potential-energy curves for four doubly charged dimers: Ag_2^{2+}, Cd_2^{2+}, Au_2^{2+}, and Hg_2^{2+}.

For the gold dimer our computations shows that the difference between the density-functional theory (DFT) in the local-density approximation (LDA) and the quantum chemical methods is less severe than previously thought. The difference is further reduced by the introduction of nonlocal corrections (gradient corrections[10,11]) to the exchange-correlation functional.

Already at the LDA level, the potential-energy curve for Ag_2^{2+} is monotonically repulsive, and it is apparent that this dimer cannot exist as a metastable system in the ground state. For Cd_2^{2+} and Hg_2^{2+}, instead, there is a substantial metastability range, with an important fission barrier and a very long lifetime. Gradient corrections reduce the estimate for the fission barrier and the lifetime, but do not change the qualitative picture.

According to DFT,[12] the total energy for a dimer with internuclear separation R is the minimum of the functional

$$E[R|\rho]=\sum_i f_i\langle\psi_i|-\tfrac{1}{2}\nabla^2+\tfrac{1}{2}V_H+\hat{V}_{\mathrm{ps}}|\psi_i\rangle + E_{\mathrm{XC}}[\rho]+E_{\mathrm{ions}} ,$$

where ρ is the valence-electron density, $\{\psi_i\}$ and $\{f_i\}$ are the Kohn-Sham eigenfunctions and their occupation numbers, respectively. V_H is the Coulomb-Hartree potential. $\hat{V}_{\mathrm{ps}}$ is the sum of the atomic pseudopotentials of the *ab initio*, norm-conserving, semirelativistic type. $E_{\mathrm{xc}}[\rho]$ is the exchange-correlation functional, here approximated by two closely related schemes: the well-known local-density approximation (LDA) and the gradient-corrected (GC) scheme. For the GC computation we used the semi-empirical exchange correction by Becke[13] and the correlation correction by Perdew.[14] E_{ions} is the potential energy of the two cores with valence charge Z_v at internuclear separation R. We took $Z_v=11$ for the IB elements, and $Z_v=12$ for the IIB elements, including in the valence charge the electrons from the s and d atomic levels of highest energy. The LDA pseudopotentials have been taken from Ref. 15, while we generated those used for the GC computations according to the prescriptions of Ref. 16.

The computational method has been described elsewhere,[17] and already successfully applied to study dimers of the IIA, IB, and IIB groups.[16,17] We briefly remember that the dimer under consideration is enclosed in a cylindrical unit cell of height L and diameter $D=L$, periodically repeated along the z direction (where z is the common symmetry axis of the dimer and of the unit cell).

The Kohn-Sham eigenfunctions $\{\psi_j(\mathbf{r})\}$ are expanded in a complete and orthogonal set of cylindrical waves:

$$\psi_j(\mathbf{r})=e^{\pm im\varphi}\sum_{G_r}\sum_{G_z}C_j(G_r,G_z)e^{iG_z z}J_m(G_r r)\ . \qquad (1)$$

(r,z,φ) are cylindrical coordinates, m is the azimuthal quantum number of the state j, J_m is the Bessel function of the first kind and order m, G_r, G_z are wave vectors selected by the imposed boundary conditions. This choice of the basis functions, and the efficient iterative algorithm (described in Ref. 17) used to determine the $\{\psi_j\}$, allow an accurate determination of the bonding properties of dimers, with a very limited error due to truncation of the basis set. A major disadvantage of this algorithm, in the case of charged systems, is represented by the periodic boundary conditions along the z direction. Because of the Ewald sum, the potential energy of two positive charges in the box is both shifted (there is no natural zero in the Coulomb potential as in the free-boundary case) and distorted at distances comparable to $L/2$.

To overcome this problem we took very large boxes, whose half-lengths $L/2$ were significantly larger than the expected distance of chemical interaction between the ions. To reduce the cost of the computation, we first optimized the wave function within a small box. Then, we rigidly transferred these wave functions in boxes of increasing dimensions, repeating the optimization at every change of unit cell. In the LDA computation the final box for Ag and Cd had $L=96$ a.u., and $L=112$ a.u. for Au and Hg. In the GC computation we stopped at $L=48$ a.u. in the case of Ag and Cd, and at $L=56$ a.u. Au and Hg. We estimate the error on the computed fission barrier Δ to be less than 0.05 eV.

The LDA potential-energy curves are reported in Figs. 1 and 2. That for Ag is monotonic, without any tendency to local minima. Those for Cd and Hg, instead, have a large region of metastability. $V(R)$ has a local minimum at $R=5.04$ a.u. for Cd and $R=4.90$ a.u. for Hg, then it bends upwards and reaches a local maximum at $R=8.48$ a.u. for Cd and $R=8.04$ a.u. for Hg. The LDA fission barrier is of 0.9 and 1.1 eV for Cd and Hg, respectively. Given the large mass of Cd and especially of Hg, the WKB approximation predicts a huge lifetime for these metastable dimers.

The most interesting result is that for Au. Also in this case the LDA curve displays a region of metastability, with, however, a fission barrier of only 0.1 eV. Given again the large mass of Au, this barrier is still enough to provide a lifetime of 6×10^{26} sec for the dimer in the vibrational ground state. With a vibrational temperature of few hundred K, the dimer might still be observable.

In view of the well-known tendency by LDA to overestimate binding, and of the low value of the fission barrier, it is important to assess the effect of the major approximations made in the computation.

The first check concerned the reliability of the pseudopotential. In the procedure of Ref. 15, pseudopotentials

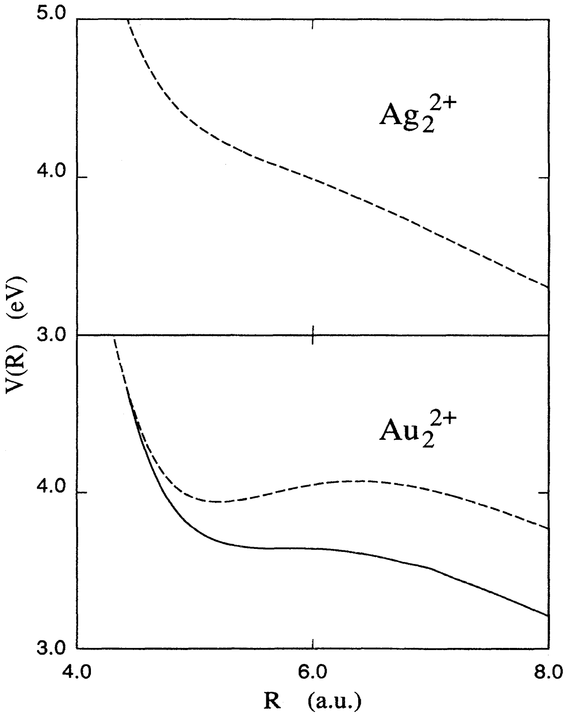

FIG. 1. Potential-energy curves for $Ag_2{}^{2+}$ and $Au_2{}^{2+}$ computed in the LDA (dashed line) and in the GC approximation (full line).

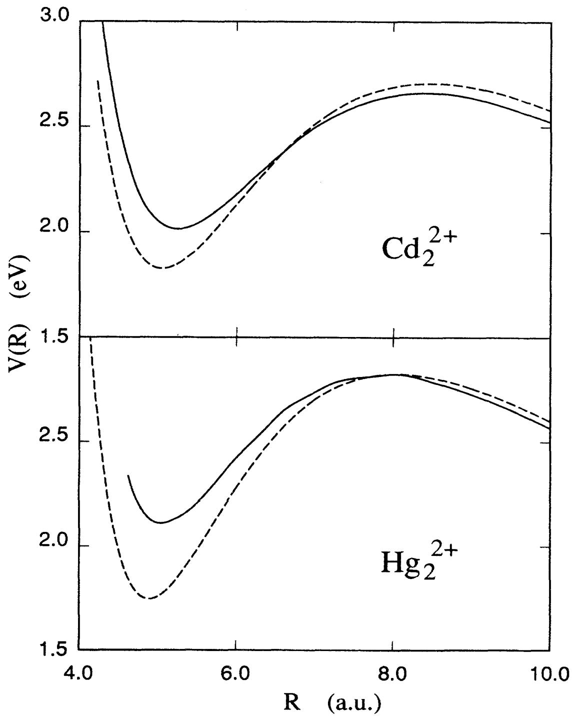

FIG. 2. Potential-energy curves for $Cd_2{}^{2+}$ and $Hg_2{}^{2+}$ computed in the LDA (dashed line) and in the GC approximation (full line).

are generated starting from a suitable atomic configuration, and their validity (or, better, the validity of the underlying frozen-core approximation) extends over a finite energy range. Experience shows that the amplitude of this range is of the order of 1 Ry. Since the ionized state is at the limit of this interval, we recomputed the pseudopotential for gold by choosing the singly ionized atomic state as reference configuration. The result for $V(R)$, however, was almost indistinguishable from the previous one.

Of course, the most important question concerns the reliability of LDA in estimating bonding energies as low as 0.1 eV. As mentioned above, we analyzed this point by adding gradient corrections to the LDA exchange-correlation functional. The effectiveness of this prescription in improving theoretical estimates for small molecules has already been verified for the IIB homonuclear dimers. Here we check their performances by computing the bonding properties of Au_2 and $Au_2{}^+$. In Table I we compare theoretical and experimental values. This comparison confirms that also in this case the GC scheme provides a significant improvement over LDA. The GC potential-energy curve for $Au_2{}^{2+}$ is displayed in Fig. 1, where it is compared to the LDA result. GC schemes reduce the short-range bonding and the fission barrier (<0.01 eV) is now well within the global uncertainties of the computation. The same method has been applied to compute the potential-energy curves for $Cd_2{}^{2+}$ and $Hg_2{}^{2+}$ (see Fig. 2). Also in this case the fission barrier is reduced ($\Delta=0.65$ eV for Cd and $\Delta=0.7$ eV for Hg), but remains sizable. Again, the WKB estimate for the lifetime is astronomically large.

Before discussing the relevance of our results for experiments, we stress that our spin-unpolarized computations do not reproduce the correct dissociation limit for $Cd_2{}^{2+}$ and $Hg_2{}^{2+}$. These dimers, in fact, dissociate in singly charged, spin-$\frac{1}{2}$ ions, and our approximation implies an overestimate of their potential energy at large distances. If the crossover to spin-polarized fragments occurs around the local maximum of $V(R)$, this error could severely affect our estimate for Δ. Unfortunately, a direct check by a spin-unrestricted computation for the doubly charged dimers would be expensive to perform. For an indirect test, we have computed the GC spin unrestricted energy E_u and the spin restricted E_r for a single ion. The difference $E_r - E_u$ is 0.25 eV for Cd^+ and 0.23 eV for Hg^+. If we take twice the difference $E_r - E_u$ as an upper bound for the error due to the spin-unpolarized approximation, we see that this is not able to change the qualitative picture described above, although it could significantly reduce our estimate for the fission barrier.

TABLE I. Bonding parameters of Au_2 and $Au_2{}^+$ computed in LDA (Ref. 16) and GC approximation, compared to the available experimental results (Ref. 18).

Dimer		r_e (a.u.)	D_e (eV)	ω_e (cm^{-1})
Au_2	LDA	4.63	3.25	193.2
	GC	4.70	2.68	174.4
	Expt.	4.67	2.30	191
$Au_2{}^+$	LDA	4.77	3.07	157.0
	GC	4.91	2.54	121.4

In conclusion, we have computed potential-energy curves for four doubly charged dimers of the IB and IIB groups of the Periodic Table. These computations, performed within the pseudopotential - DFT framework and using the LDA and GC approximations for the exchange and correlation energy, show that $Ag_2{}^{2+}$ is unstable in the ground state. The $Au_2{}^{2+}$ dimer, weakly metastable within the local-density approximation, is predicted to be practically unstable ($\Delta<0.01$ eV) when gradient corrections are introduced. This result, in agreement with the quantum chemistry computations,[5,6] suggests that the experimental observation of $Au_2{}^{2+}$ probably concerned molecules not in their ground state.

The doubly charged IIB dimers $Cd_2{}^{2+}$ and $Hg_2{}^{2+}$, instead, are predicted to be metastable, with a sizable fission barrier. Even taking into account the error implicit in our spin-unpolarized computation, the computed value of Δ should be enough to ensure the detectability of these species.

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