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Bonding properties of mercury dimers in the pseudopotential local-density-approximation scheme

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Bonding properties of the mercury dimers Hg_2 and $Hg_2{}^+$ are investigated with accurate computations carried out in the density-functional local-density-approximation (LDA) scheme, within the pseudopotential framework. Our calculation accounts for several characteristic properties of these molecules, without, however, full quantitative agreement with experiment. Nevertheless, we argue that the pseudopotential LDA scheme provides a suitable model to study the size evolution in the electronic structure of mercury clusters. Furthermore, the investigation of such systems containing a large number of atoms may be simplified, by including in the valence charge the $6s$ electrons only, and properly taking into account the short-range repulsion of the filled $5d$ shells.

Small aggregates of transition-metal atoms are currently of great interest for the variety of their chemical behavior and their relevance to important technological processes.[1] Among them, special attention has been devoted to mercury clusters.[2–4] Following early theoretical speculations,[2] recent spectroscopic measurements[3,4] have documented for the first time the gradual transformation with size of the bonding character in these systems: For $2 \leq N \leq 8$ they appear to be weakly bound van der Waals clusters, whereas the gradual onset of metallic character is observed in the range $N = 20$–80 (N indicates the number of atoms).

The theoretical investigation of this transition faces a formidable double challenge: (i) of principle, for the importance of many-body and relativistic effects; and (ii) computational, for the large number of electrons involved in the chemical bond, the strong electron-ion potential, the difficulties in achieving self-consistency between the charge density and the potential in *ab initio* calculations. Moreover, for $N > 5$–6, the determination of the equilibrium ionic structure is an additional demanding problem.

As a first step in a systematic analysis of these problems, we present here the results of a computation of the bonding properties of Hg_2 and $Hg_2{}^+$, performed in the pseudopotential local-density approximation[5] (LDA). In order to accurately describe the electronic properties of linear molecules, we have implemented a new algorithm, with two main innovative features. The LDA molecular orbitals are expanded in an orthogonal and complete basis set (cylindrical waves) adapted to the symmetry of the Hamiltonian. The large number of basis functions required by the expansion is dealt with an efficient iterative procedure.

Important qualitative features characterizing the mercury dimers are correctly reproduced by the present model, suggesting that this may provide a useful tool to study the size evolution of the electronic properties of mercury clusters. Nevertheless, we find some quantitative discrepancies with experiment, comparable in quality and magnitude to those found in other LDA molecular computations for transition metals.[6]

We also show that an approximation can be devised, which drastically reduces the size of the computation, while accurately retaining the physical features of interest. We believe it will allow for the numerical *ab initio* investigation of mercury clusters whose size is in the interesting range of their bonding transformation.

The starting point of our computation is the density-functional theory LDA (DFT-LDA) energy functional. The total energy of the system in its electronic ground state is

$$E[\rho] = \sum_i f_i \langle \psi_i | -\tfrac{1}{2}\nabla_i^2 + \tfrac{1}{2} V_H + \varepsilon_{\mathrm{xc}} + V_{\mathrm{ps}} | \psi_i \rangle + H_{\mathrm{ions}} , \tag{1}$$

where $\rho(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$ and the sums extend over the occupied independent particle orbitals ψ_i, whose occupation numbers are f_i. V_H is the Coulomb-Hartree potential. $\varepsilon_{\mathrm{xc}}$ is the exchange and correlation energy in the LD approximation.[7] The interaction V_{ps} between the ions and the valence ($5d^{10}6s^2$) electrons is described by a nonlocal pseudopotential, obtained from a first-principles relativistic atomic computation.[8] This enables us to take into account scalar relativistic effects. H_{ions} is the classical Hamiltonian of the ions. The full Hamiltonian (H) has $D_{\infty h}$ symmetry and the orbitals ψ can therefore be chosen to be eigenstates of rotations around the axis (z) of the molecule:

$$\psi_i(\mathbf{r}) = e^{\pm i m \varphi} \phi_i(r,z) , \tag{2}$$

where (r,z) are cylindrical coordinates and m is the azimuthal quantum number. The system is enclosed in a cylinder of height $2a$ and radius R. Each orbital is expanded in a basis set of cylindrical waves:

$$\psi_i(\mathbf{r}) = e^{\pm i m \varphi} \sum_{G_r} \sum_{G_z} C_i(G_r, G_z) J_m(G_r r) e^{i G_z z} , \tag{3}$$

where J_m is the Bessel function of the first kind of order

m. Periodic boundary conditions are imposed in the z direction, with periodicity $2a$. The boundary condition at $r=R$ $[\psi(R,z)=0,\ -a\leq z\leq a]$ selects the allowed values of G_r.

As suggested in Ref. 9, $E[\rho]$ is minimized by computing the gradients $\partial E[\rho]/\partial C_i^*(G_r,G_z)$, and evolving the coefficients $C_i(G_r,G_z)$ in time, according to the following equation of motion:

$$\dot{C}_i(G_r,G_z)=-\frac{\partial}{\partial C_i^*(G_r,G_z)}(E[\rho]-\varepsilon_i\langle\psi_i\,|\,\psi_i\rangle)\,. \qquad (4)$$

The ε_i are Lagrange multipliers that ensure the orthonormality of the orbitals. A detailed description of the algorithm will be given elsewhere. Here we want only to underline its distinctive features. By using a set of basis functions adapted to the symmetry of the system, the expansion (3) makes it possible to reduce a three-dimensional problem to an effective two-dimensional (2D) computation. (Different approaches to 2D expansions of molecular orbitals for dimers are described, e.g., in Ref. 10.) Furthermore, the iterative scheme, which avoids the storage and the direct diagonalization of H, makes feasible a computation with a large set of basis functions (up to 2048 for the expansion of the ψ's in the present study).

In our calculation we have chosen $a=14$ a.u. and $R=14$ a.u.; in Eq. (3) we have included cylindrical waves up to a kinetic energy cutoff (E_{cut}) of 51.6 Ry, corresponding to a charge-density cutoff of 206 Ry. We have checked the convergence with respect to E_{cut} by repeating the computation for few r separations with $E_{\text{cut}}=70$ Ry. The difference between the cohesive energy (D_e) obtained in the two computations is of a few meV. The integration of Eq. (4) with the largest E_{cut} required 2-3×10^3 steps, the time step being set at 3×10^{-3} a.u.[11] The iterative procedure was stopped when the energy variation per step was less than 4×10^{-7} Ry. In the case of $\text{Hg}_2{}^+$, the net charge has been neutralized by a negative uniform background. Special attention has been paid to control the interaction between periodic replicas. Our estimate for its effect on the cohesive energy curve of $\text{Hg}_2{}^+$ is of the order 5×10^{-3} eV.[12]

In Figs. 1 and 2 we present the results for the cohesive energy of Hg_2 and $\text{Hg}_2{}^+$. The parameters characterizing the bonding are summarized in Table I. Experimental bond lengths (R_e) are reasonably well reproduced by our computation; cohesive energies and vibrational frequencies are instead greatly overestimated. The excitation and ionization energies are both underestimated by about 1 eV. In spite of quantitative discrepancies with the available measurements, the qualitative agreement between our model and experiment is good. Indeed, we find a weakly bound neutral molecule, with a large equilibrium distance and a relatively low vibrational frequency. More importantly, the lowest unoccupied molecular orbital, coming from the bonding combination of the atomic $6p$ levels, is 4.5 eV above the highest occupied level. This large gap is an indication of the "insulating" character of Hg_2. It would be of the greatest interest to study the evolution of this property with an increasing number of atoms in the cluster, and its sensitivity to the ionic geometry.

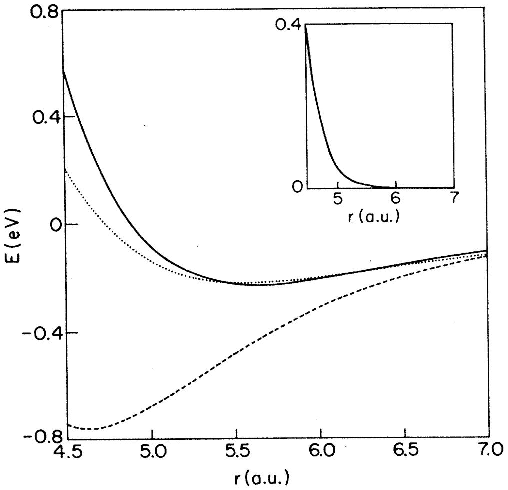

FIG. 1. Potential-energy curve of Hg_2. Solid line: ($5d6s$) computation. Dotted curve: ($6s$ + NLCC) computation. Dashed line: ($6s$) computation. The difference $V(r)$ between the ($5d6s$) and ($6s$ + NLCC) is plotted in the inset.

In order to simplify this task, we have explored the possibility of including in the valence charge only the electrons occupying the $6s$ atomic levels. In fact, the subdivision of the total charge in core and valence contributions is somewhat ambiguous for Hg, since its $5d$ levels are completely filled. From a computational point of view, the inclusion of d electrons in the core is an appealing possibility: It reduces the number of valence electrons (VE) by a factor of 6, and—more important—the potential and charge density are much smoother, resulting in a smaller E_{cut} required for expansion (3). As an additional advantage, a reduced cutoff usually corresponds to a faster and more stable convergence of the iterative algorithm to the total energy minimum.

However, the $5d$ and $6s$ atomic levels occupy virtually

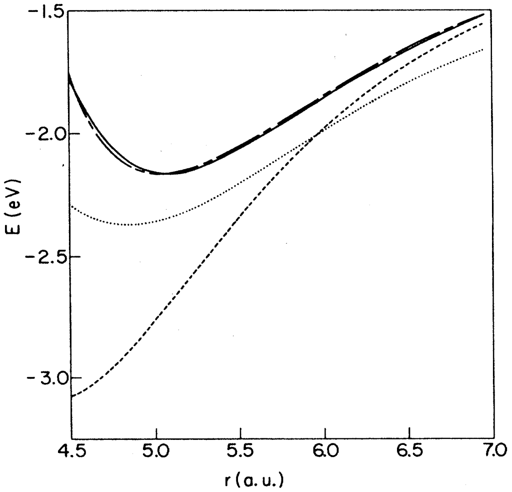

FIG. 2. Potential-energy curve for $\text{Hg}_2{}^+$. Solid line: ($5d6s$) computation. Dotted line: ($6s$ + NLCC) computation. Dashed line: ($6s$) computation. Dashed-dotted line: ($6s$ + NLCC) potential-energy plus two-body contribution $V(r)$, rigidly shifted (see text).

TABLE I. Comparison between computed (LDA, present calculation) and measured (Expt.) bonding properties of Hg_2 and Hg_2^+: bond distance (R_e) and energy (D_e), vibrational frequency (ω), vertical (VIP) and adiabatic (AIP) ionization potentials, and energy difference between the lowest unoccupied molecular orbital and the highest occupied molecular orbital (ΔE_{L-H}). The quoted experimental value for ΔE_{L-H} is an estimate from Fig. 1 of Ref. 19.

Ground-state properties	LDA	Expt.	Reference
	Hg_2		
R_e (a.u.)	5.65	6.05	14
		5.52	15
		6.86	16
D_e (eV)	0.23	0.11	15
		0.04	16
		0.07	17
ω (cm^{-1})	74	44	15
		18.5	16
		36	17
VIP (eV)	8.40	9.10	18
AIP (eV)	8.20		
ΔE_{L-H} (eV)	4.50	5.5	19
	Hg_2^+		
R_e (a.u.)	5.08		
D_e (eV)	2.20	1.40	19
ω (cm^{-1})	126		

the same region of space, thus implying a strong nonlinear coupling between them via exchange and correlation. In order to take this effect into account, we have derived a pseudopotential and the corresponding pseudo-charge-density following the scheme proposed by Louie, Froyen, and Cohen.[13] The results of this approximation for both Hg_2 and Hg_2^+ are in good agreement with those of the previous ($5d$,$6s$) computation, for distances larger than R_e. The agreement becomes worse at shorter distances where the repulsion of the d shells is clearly underestimated. To emphasize the importance of the nonlinear core corrections (NLCC), we have plotted in Figs. 1 and 2 the results of a computation with the $6s$ VE only, but without NLCC.[8] R_e of Hg_2 is now reduced to only 77% of the experimental value and D_e is an order of magnitude larger than the experiment. Given the widely different effort required by the two computations, the agreement between the ($5d$,$6s$) and ($6s$+NLCC) energy curves is impressive. However, for larger systems, the softening of the short-range repulsion in the latter scheme may affect the computed static and dynamical properties.

The difference between the energy curves relative to the ($5d$,$6s$) and ($6s$+NLCC) valence configurations $V(r)$ is plotted in the inset of Fig. 1. In the region of interest it can be fitted by a simple exponential, $V(r) = 331.675e^{-4.02(r-2)}$ (in a.u.), with an accuracy ≤ 0.02 eV. This suggests that the main effect of the d electrons is a short-range interaction with the exponential shape characteristic of the closed-shell overlap. The highest eigenvalue turns out to have the same dependence on distance, irrespective of the chosen valence configuration: This confirms the absence of significant hybridization of the d orbitals with the higher occupied levels. It is therefore reasonable to try to represent the effects of the d orbitals by the two-body potential specified above. The first check is offered by Hg_3 in the linear configuration. In Fig. 3 the dashed-dotted curve is computed by adding to the ($6s$+NLCC) energy curve the potential $V(r)$. The agreement with the computation involving both $5d$ and $6s$ electrons is very good. A different check is given by a similar calculation performed for Hg_2^+. Here the two curves differ not only in the short-range part, but also because they tend to dissociation limits with slightly different energies.[12] Once this long-range effect is taken into account by a rigid shift, the potential $V(r)$ is again able to correct very well the repulsive part of the ($6s$+NLCC) curve.

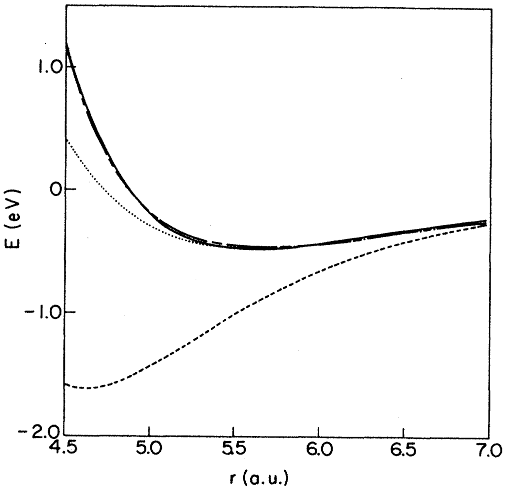

FIG. 3. Potential-energy curve of Hg_3 in the linear $D_{\infty h}$ geometry. Solid, dotted, dashed, and dashed-dotted lines as in Fig. 2.

The ability of the pseudopotential LDA scheme to describe small aggregates of mercury atoms has been tested by an accurate computation for Hg_2 and Hg_2^+, showing that the model is able to correctly reproduce several characteristic properties of these molecules. We have also shown that the $5d^{10}$ electrons can be included in the core, without compromising the description of the highest valence levels. These two conclusions together offer the possibility of approaching the problem of the van der Waals to metal transition in mercury clusters. To this aim, the *ab initio* molecular dynamics proposed by Car and Parrinello[9] appears to be the ideal tool. It allows for an effective optimization of the ionic geometry, while providing a state of the art description of the electronic structure.

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[11] A test run continued for additional 10^3 steps decreased the total energy by less than 1 meV.

[12] The experimental dissociation limit of $Hg_2{}^+$ ($Hg+Hg^+$) is not correctly reproduced by our LDA calculation. For large internuclear separations we still find a symmetric distribution of the charge on the two ends of the dimer. Here, D_e of $Hg_2{}^+$ is referred to the sum of the energies of Hg and Hg^+, obtained in two separate computations.

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