tational state. From the rotational state distribution measured, one can calculate the percentage of OH radicals formed in the various rotational states. This, together with the measured population inversions in the beam gives a final ratio of ~4:1 for the Λ doublets of the ($^2\Pi_{3/2}$, $v=0$, $J=1.5$) state. Because this inversion is at least two times larger than ratios assumed by others, it clearly shows the feasibility of this simple mechanism.

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Metal-Metal Bonding in Cr-Cr and Mo-Mo Dimers: Another Success of Local Spin-Density Theory

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Self-consistent local-spin-density total-energy calculations for Cr_2 and Mo_2 yield $^1\Sigma_g{}^+$ ground states with dissociation energies and equilibrium bond lengths in excellent agreement with experiment—in marked contrast with the results of a generalized-valence-bond–van der Waals approach, which used 26 512 determinants, and previous local-density efforts. The present results indicate the reliability of local spin-density theory for very inhomogenous systems, when sufficient variational (and symmetry) freedom is included.

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The local density (LD) functional theory[1] is now the most widely used theoretical approach for determining the electronic structure of materials. Its great utility derives from the accurate experimental predictions obtained in systematic and extensive theoretical investigations of the electronic structure and properties of molecules and a wide variety of bulk solids and surfaces. The one striking exception—and indeed perhaps its outstanding failure—lies in the apparent inability of LD theory to describe properly the nature of the metal-metal bonding in such seemingly simple systems as the transition-metal (TM) dimers.[2] A recent Letter[3] presented potential curves for the Mo_2 and Cr_2 dimers determined from a generalized valence-bond approach that includes correlations for the van der Waals interactions (GVB-vdW). These results, based on a wave function for the $^1\Sigma_g{}^+$ state containing 26 512 slater determinants involving 18 valence molecular orbitals, disagreed dramatically with those from the earlier LD calculations[2] and "cast doubt on the efficacy of the local (spin) density approximation in calculations on transition metal systems."[3]

The TM dimers pose a severe test for LD theory, which uses an exchange-correlation function derived from the many-body descriptions of the interacting electron gas and hence is not expected, in principle, to be applicable in the limit of highly localized electrons in free atoms and diatomic molecules. Its apparent failure[2,3] to predict correctly the ground-state symmetry, binding energy, and bond length of the Cr_2 molecule cannot be dismissed lightly. For this reason, we have carried out and report here results of highly accurate self-consistent full-potential local-spin-density (LSD) calculations for Cr_2 and Mo_2. Our total-energy calculations show the ${}^1\Sigma_g{}^+$ state to be the ground state in both dimers; no double-well potential is found for Mo_2 (as previously reported[3]) or for Cr_2. Our calculated values of the dissociation energy, D_e, and bond lengths, R_e, which disagree markedly with the earlier theoretical results,[2,3] are in excellent agreement with experiment for both Cr_2 and Mo_2 and thus represent a triumph of LSD theory. In addition, these results call attention to the actual failure of the GVB-vdW approach[3] to predict correctly both D_e and R_e in Cr_2 and D_e in Mo_2 and so cast doubt on the validity of this approach for correctly describing the bonding of TM dimers.

The important simplification and approximation of LSD theory is to replace the many-body Hamiltonian by an effective single-particle Hamiltonian[1] with an exchange and correlation effective potential taken from accurate many-body calculations for the homogeneous interacting electron gas. In the self-consistent multipolar method used here[4] LD equations are solved variationally using, for Cr, neutral-atom numerical 3*d*, 4*s*, and for Cr^{2+}, 3*d*, 4*s*, and 4*p* functions as a basis set. Cr 3*s* and 3*p* semicore functions were included in the variational valence space, since there is appreciable overlap with the neighbor atom at the short bond lengths occurring in Cr_2. Deep-level core functions were frozen and the valence basis functions were Schmidt orthogonalized against the core functions—an approximation verified to not affect the binding energy or one-electron eigenvalues. Corresponding basis sets were used in the Mo_2 case.[5] For the Coulomb potential, results which are highly converged were obtained by representing the charge distribution by overlapping multipoles with[4] $l \leq 2$. For the effective spin-dependent exchange and correlation potential we used the formulation of von Barth-Hedin.[6] Variational secular equations were solved iteratively for both spin directions.

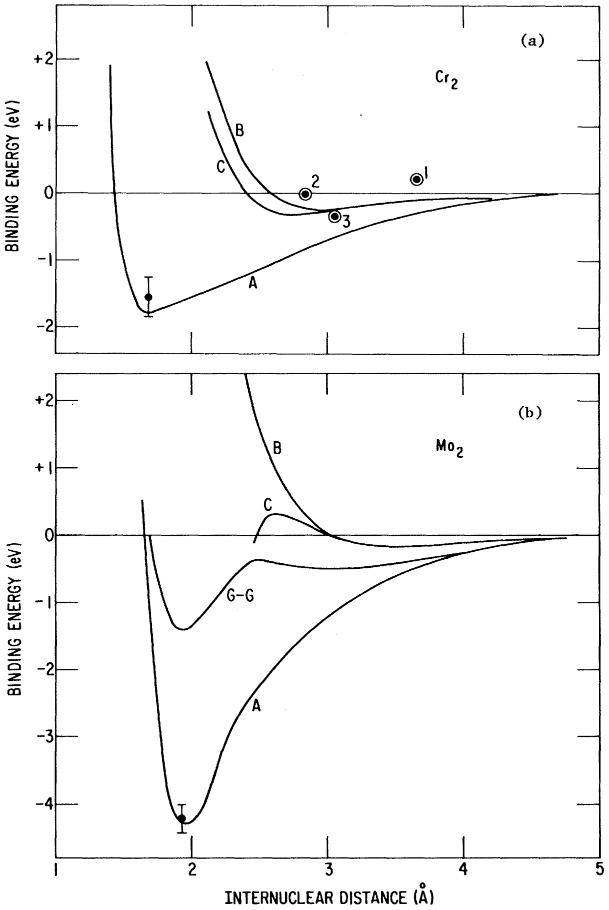

FIG. 1. Theoretical binding energy vs internuclear distance for (a) Cr_2 and (b) Mo_2 dimers. Curve *A* represents the ${}^1\Sigma$ antiferromagnetic state; curve *B*, the ${}^{13}\Sigma$ excited state. The energy for ferromagnetic spin alignment is shown in curve *C*. For Cr_2, the points labeled (1) and (2) are the ${}^{13}\Sigma_g$ and ${}^{11}\Sigma_u$ energies from Ref. 2, respectively. Point (3) is the ${}^1\Sigma_g$ result of Ref. 3, and the solid point with error bars denotes the experimental value of Refs. 8 and 9. For Mo_2 the curve *G-G* denotes the ${}^1\Sigma_g$ result of Ref. 3, and the experimental value of Refs. 9 and 10 is shown by the solid dot.

It is important to observe that the symmetry of the single-particle Hamiltonian may be lowered when the spin density is nonvanishing and that reducing the $D_{\infty h}$ symmetry of the homonuclear dimer to $C_{\infty v}$ symmetry for solving the secular equations will not predetermine whether the self-consistent spin density will have $C_{\infty v}$ or $D_{\infty h}$ symmetry; it represents an implicit degree of freedom in the calculation.

The results of our binding-energy calculations as a function of bond length are given in Fig. 1. We find in both dimer molecules that the ground state is "antiferromagnetic" (AF) with $M_S = 0$ at all bond distances considered. The equilibrium-bond-length configuration of Cr_2 is $(1\sigma_{A,d}\uparrow)$-

$(1\sigma_{B,d}\downarrow)(\pi_{A,d}\uparrow)^2(\pi_{B,d}\downarrow)^2(2\sigma_{A,s}\uparrow)(2\sigma_{B,s}\downarrow)(\delta_{A,d}\uparrow)^2(\delta_{B,d}\downarrow)^2$. Here ↑, ↓ refers to the spin orientation, A,B refer to the two atom sites, and s,p,d refer to the atomic one-electron state from which the orbital is mainly derived.

As is well known, LSD theory does not determine a well-defined (unique) many-electron state function. In the present case, it is clear that the exchange of labels $A \leftrightarrow B$ produces an entirely equivalent electron configuration; i.e., at least two determinants are required to form a true AF configuration: $(\uparrow\downarrow - \downarrow\uparrow) = {}^1\Sigma(M_S = 0, S = 0)$ and $(\uparrow\downarrow + \downarrow\uparrow) = {}^3\Sigma(M_S = 0, S = 1)$. In general, the LSD total energy E_t is an approximation to some particular average over multiplet energies built upon the given single-particle configuration. For special cases, e.g., M_S = maximum (6 in the present case), there is a unique single-determinant wave function and E_t is expected to give a good approximation to the state energy. For the ground configuration, which we find with $M_S = 0$, $E_t(R)$ may contain not only the lowest ${}^1\Sigma$ energy, but also an R-dependent contamination arising from states built on the self-consistent configuration. To assess the weight of ${}^{2S+1}\Sigma$ states, it is always possible to carry out self-consistent calculations with the constraint $M_S = S, S-1, S-2 \ldots$. This is the basis for successful determination of multiplet splittings.[7]

Spin-unrestricted theory leads to a maximal spin compatible with the ground state; this eliminates admixtures of lower-spin excited states and leads to an increase in binding energy. (This happens for the Cr and Mo atoms where $M_S = 3$ is found.) On this basis, and considering the magnetic point group $D_{\infty h}$ with unitary subgroup $C_{\infty v}$, we identify the ground configuration with the ${}^1\Sigma_g{}^+$ state, and recognize the possibility of slight contamination from higher multiplets which would reduce the binding energy.

We find that for both Cr_2 and Mo_2, the ground configuration has $M_S = 0$ (AF state) at all bond lengths. In Cr_2, at 3 Å separation, the spin density is atomiclike on each site, becoming reduced around 2 Å, and vanishing entirely at 1.6 Å. Our calculated D_e (1.80 eV) and R_e (1.70 Å) are in excellent agreement with experiment (1.56 ± 0.3 eV[8] and 1.69 Å,[9] respectively). Because of the rather anharmonic nature of the curve near R_e, a parabolic fit gives only a crude estimate of the vibrational frequency, $\omega_e = 450\ \mathrm{cm}^{-1}$. The high-spin $M_S = 6$ configuration is considerably less bound at all R, and is repulsive for $R < 2.6$ a.u. The symmetry-restricted "ferromagnetic" $D_{\infty h}$ result is similarly weakly bound, and becomes repulsive for $R \gtrsim 2.3$ a.u.

Of the many low-lying excited states available to Cr_2, the ${}^{13}\Sigma_g{}^+$ is compatible with dissociation of the spin density to the isolated atom's spin density. In addition, ambiguities due to multideterminant states can be avoided by searching for the ground state with the constraint $M_S = 6$, shown in Fig. 1 (curve B) to possess a shallow minimum (−0.25 eV) near 3 Å. Further, upon restricting the spin density to be compatible with $D_{\infty h}$ symmetry (curve C) we approach the binding energy of the ${}^{13}\Sigma_g{}^+$ state (curve B) at large R. For $R < 3$ Å, the ferromagnetic spin density (curve C) is found to be reduced and to yield more binding energy than does curve B. For $R < 2$ Å, curve C drops dramatically (not shown in Fig. 1), the spin is rapidly reduced upon closer approach, and the binding energy increases greatly and approaches curve A at 1.69 Å where the spin density disappears completely.

The results given in Fig. 1 for Mo_2 are similar to those for Cr_2: the "antiferromagnetic state" ${}^1\Sigma_g{}^+$ has $D_e = 4.35$ eV, $R_e = 1.95 \pm 0.05$ Å, and $\omega_e = 520 \pm 50\ \mathrm{cm}^{-1}$ in rather good agreement with experimental values of 4.20 ± 0.2 eV,[10] 1.93 Å,[9] and 477 cm^{-1},[9] respectively.

We also show in Fig. 1 the result of the earlier LD study,[2] which led to assignment of the ${}^{11}\Sigma_u{}^+$ state as the Cr_2 ground state; labeled as point (2) in Fig. 1(a) it lies close to the minimum in our LSD result for ferromagnetic alignment (curve B). This result is not surprising since spin polarization was introduced only as a perturbation after self-consistency was achieved for the paramagnetic (non-spin-polarized) state.[2] Evidently, the result of a paramagnetic calculation leads to $D_{\infty h}$ symmetry, which corresponds to the ferromagnetic state; it further suggests that it is not possible by means of perturbation theory to obtain accurate predictions about the nature of the "antiferromagnetic" (${}^1\Sigma_g{}^+$) ground state. In view of the excellent agreement with experiment obtained in our LSD calculation, we can conclude that the "failure of LD theory"[3] in the case of Cr_2 is attributable to the use of perturbation theory to obtain spin-dependent energies and not to anything intrinsic in LD theory itself.

Comparing our results with those of GVB-vdW theory[3]—shown in Fig. 1—we see large disagreements for both Cr_2 and Mo_2. For Cr_2 both D_e and R_e disagree markedly with the LSD predictions *and* with experiment; D_e is too low in energy by a factor of 5 and R_e is off by a factor of 2. For

Mo_2, R_e for the $^1\Sigma_g{}^+$ ground state is predicted accurately by the GVB-vdW result but D_e is again too low (by a factor of 3). It has been argued[3] that the experimental D_e (Ref. 10) might be too large due to misinterpretation of the Knudsen cell measurement caused by neglect of excited states of Mo_2 or to nonequilibrium conditions. To us it seems unlikely that such conditions might have affected the spectroscopic measurement of $D_e = 4.1 \pm 0.7$ eV (Ref. 9) in the same way. Therefore, we propose that the experimental D_e (Ref. 10) (4.2 ± 0.2 eV) be taken seriously. Accepting this value and $\omega_e = 477$ cm^{-1}, it also seems unlikely that Mo_2 has a double-well potential as determined by the GVB-vdW method, but not found here.

These results give a striking picture of the subtle interplay between exchange and bonding in multiple-bonded magnetic molecules. For the Cr_2, $M_S = 0$, AF ground state, there is very little overlap between the two Cr atoms at large R. For $M_S = 6$, spin alignment requires occupation of antibonding levels at small R; so, in order to retain most of the spin energy, the weights of the atomic components building up the molecular orbital are modified in such a way that the occupied orbitals reside mostly on the atom with favorable spin direction. At small R, overlap charge becomes more important as a contributor to the binding energy and the spin energy is consequently reduced. At R_e all spin orbitals have become nearly mirror symmetrical (bonding orbitals) about midbond, but still it is advantageous to retain a part of the spin energy. Thus, this situation can be described (with small reservations in view of the nonzero spin-energy contributions) as a sextuple bond. A separate spin-restricted calculation on Cr_2 at R_e gives a binding energy 0.1 eV less than that of the unrestricted case, demonstrating the rather small contributions of spin energy at R_e. Finally, we observe that for $R > 2.2$ Å the bonding is predominantly of $\sigma(s)$ type. Near 2 Å, d multiple bonding rapidly increases in importance, beginning with the $\sigma(d)$ orbital and followed by the $\pi(d)$ and finally the $\delta(d)$ orbital. Despite the dramatic changes in internal structure, multiple bonding sets in so gradually that no humps (double wells) can be seen in the binding-energy curve.

Qualitatively similar results were obtained for Mo_2. The smaller spin-energy contributions (4.4 eV for the free Mo atom versus 5.4 eV for Cr) help to explain the higher D_e of Mo_2 by assuming an approximately constant bonding energy. In contrast to Cr_2 the Mo_2 curve shows a small shoulder at 2.3 Å where multiple bonding becomes important. The reduction of the well found in Ref. 3 to a mere shoulder is particularly striking. A deeper well could have been obtained here by restricting the variational freedom as evidenced, e.g., by the Mo_2 $D_{\infty h}$ calculations. Possible candidates for accidental restrictions in the GVB-vdW theory[3] include their use of only 18 valence orbitals—in constrast with our use of 30 valence functions. In addition, we find that Mo $4s,4p$ semicore states, treated as part of the pseudopotential core in Ref. 3, overlap appreciably—an effect not treated in the pseudopotential approach.

In conclusion, we have found that local spin-density theory yields accurate predictions for the energetics of bonding in transition metal dimers, in marked contrast to the GVB-vdW approach.[3] The self-consistent multipole local density method[4] allows much larger clusters to be treated without undue restriction on, for example, basis sets. Recently successful studies have been made on molecular clusters containing up to 79 Cu metal atoms.[11]

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