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Density-functional study of niobium clusters

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We describe local and nonlocal Gaussian orbital-spin-polarized density-functional calculations for clusters of two to seven niobium atoms. The most stable geometries found with geometry optimization have a high atomic coordination. The trends in the experimental binding energies, bond dissociation energies, and ionization potentials are well reproduced with the exception of the pentamer bond dissociation energy, which is too low. The possible causes are discussed. These are the most extensive *state-of-the-art* calculations to date for the clusters of a transition metal.

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The ground-state atomic and electronic structure of small clusters poses a considerable challenge for modern quantum chemistry. Density-functional theory and related techniques have had considerable success for the lighter elements. The preferred stable geometries have been determined for lithium [1], beryllium [1], sodium [2], aluminum [3], and silicon [4] among others. The calculated binding energies, bond dissociation energies, and ionization potentials are generally in good agreement with the experimental values (see, for example, [5] for a review). However, for the transition metals only the dimer, the trimer, and sometimes the tetramer have been accurately studied.

In this Rapid Communication, we demonstrate that the stable geometries of transition-metal clusters are accessible to *state-of-the-art* theoretical techniques. We describe extensive density-functional calculations for clusters of niobium containing up to seven atoms. Stable geometries are found and the atomic structure described. The energetics for the most stable are compared with experiment and, as we shall see, the calculations lead to a good reproduction of the qualitative features of the experimental data, consistent with the results for lighter elements.

The total energy and the atomic forces were calculated with an accurate spin-polarized density-functional method [8–10], using both local [11] and nonlocal [12] exchange-correlation potentials and model core potentials to describe the niobium atoms. The atomic cores were described with a $1s^2 2s^2 3s^2 4s^2 2p^6 3p^6 3d^{10}$ configuration corresponding to a valence space of 11 electrons. The screened potential and the Gaussian orbital basis for the valence electrons were optimized [13] to ensure accurate reproduction of the valence energies and wave functions for the atom. Calculations with this model core potential on the dimer, the monoxide, and the mononitride reproduced to a high degree of accuracy the experimental equilibrium bond lengths, bond dissociation energies, and harmonic frequencies. Additional auxiliary bases of Gaussian orbitals were employed to describe the charge density and the exchange-correlation potential, allowing improved numerical efficiency.

The stable minima were located with repeated geometry optimizations of both low- and high-symmetry starting geometries [6], using a variant of the conjugate gradient method [7]. The total energy and atomic forces were explicitly evaluated at each updating step. Thus for a six-atom cluster approximately 100 self-consistent calculations were performed.

The dimer had a triplet ground state with spectroscopic constants, in excellent agreement with other theoretical calculations [14–16] and in reasonable agreement with the scarce experimental data [17,18]. The experimental bond dissociation energy and ionization potential are 5.2 eV (±0.30) and 5.9 eV (±0.3), respectively. The local theoretical values are 5.8 and 5.9 eV, respectively. The nonlocal theoretical bond dissociation energy is 5.4 eV, in closer agreement with the experimental value. The nonlocal ionization potential was not calculated. Recent local-spin-density calculations found an equilibrium bond length of 2.12 Å [14], while complete active-space self-consistent-field calculations found a value of 2.10 Å. Our calculation found a value of 2.08 Å, in excellent agreement with the theoretical values. The nonlocal value was somewhat larger at 2.10 Å. The above calculations found harmonic frequencies of 451 [14] and 447 cm^{-1}, in excellent agreement with our local and nonlocal values of 472 and 447 cm^{-1}, respectively.

The most stable geometries located with the local potential are illustrated schematically in Fig. 1. Atoms in equivalent positions are indicated.

The trimer adopted an isoceles triangle with sides of lengths 2.37, 2.37, and 2.26 Å and a ground-state multiplicity of 2. Ionization led to an increase in the symmetry, all bonds having a length of 2.37 Å, and a ground-state multiplicity of 3. A linear geometry was also stable though highly unfavorable, the energy being 3.2 eV higher than for the triangle. The ground-state multiplicity was 4.

The tetramer was most stable as an ideal tetrahedron with sides of length 2.47 Å and a ground-state multiplicity of 1. The tetrahedron ionized to an expanded ideal tetrahedron with sides of length 2.49 Å and a ground-state multiplicity of 2. An ideal parallelepiped was also

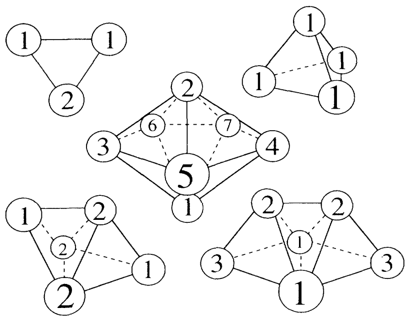

FIG. 1. The most stable geometries located. The labels indicate atoms related under symmetry-group operations of the clusters.

stable with sides of length 2.31 Å and a short diagonal of 2.61 Å with a ground-state multiplicity of 3. This geometry, which was explicitly optimized from a high-symmetry starting geometry, was less stable by 1.2 eV. The linear chain was not considered.

The pentamer was most stable in a trigonal bypyramid geometry with a ground-state multiplicity of 2. The geometry was highly symmetric with equatorial bonds of length 2.71 Å and polar-equatorial bonds of length 2.43 Å. Ionization led to a Jahn-Teller distortion, breaking the symmetry of the equatorial plane such that only two bonds were of the same length. The equatorial bond lengths were 2.79, 2.79, and 2.52 Å. The polar-equatorial bond lengths were 2.52, 2.52, and 2.79 Å. The ionization thus led to a slight expansion of the cluster. The ground-state multiplicity of the ion was 2. The pentamer was also stable as a face-capped square geometry with a ground-state multiplicity of 2. This geometry was less stable by 1.4 eV. The bonds were all of length 2.52 Å.

The hexamer was most stable in a geometry formed from a planar parallelepiped capped with a dimer, which lay parallel to the plane of the parallelepiped and aligned along the long diagonal (see Fig. 1). The parallelepiped had sides of length 2.44 Å and a short diagonal of 2.71 Å. The capping dimer atoms each lay 2.22 Å from the plane of the parallelepiped and were separated from each other by 2.31 Å. The ion had a multiplicity of 2. Also stable, though less energetically favorable by 0.26 eV, was a distorted form of the above geometry. The parallelepiped was no longer planar, having buckled about the short diagonal. The buckling brought the two atoms forming the short diagonal closer to the capping dimer, which itself had also rotated by a small angle about an axis normal to the original plane of the parallelepiped. This geometry can also be seen as a distorted octahedron in which the equatorial bond lengths are 2.44, 2.61, 2.61 and 3.55 Å; the polar-equatorial bond lengths are 2.44, 2.46, 2.49, and 2.83 Å for each polar atom; and the polar-polar bond length is 3.07 Å. Thus the octahedron has deformed so as to bring the polar atoms closer together, at the expense of the equatorial bonds, one of which has a length of 3.55 Å and is thus weak. The ground state had a multiplicity of 3. A third stable geometry, lying 0.43 eV higher in energy than the dimer capped parallelepiped, resembled a highly distorted octahedron, with the equatorial atoms defining an irregular polygon with sides of lengths 2.63, 2.63, 3.02, and 4.00 Å. the polar-equatorial bond lengths were in all cases equal to 2.49 Å while the polar-polar bond length was 2.98 Å, suggesting a high degree of bonding between the polar atoms. This geometry is similar to the preceding one, with the notable difference that it has only two strong equatorial bonds (as opposed to three) and thus might be expected to be less favorable, as is the case. The ground-state multiplicity was 3.

The heptamer was most stable in a distorted pentagonal bipyramid geometry. The principal distortion from the ideal geometry was the displacement of one of the atoms in the equatorial pentagon along a direction perpendicular to the equatorial plane. The equatorial bond lengths were 2.51, 2.51, 2.52, 2.52, and 2.53 Å, while for the polar-equatorial bonds the values ranged from 2.43 to 2.84 Å. The polar-polar bond length was 3.12 Å and thus reasonably strong. The ground-state multiplicity was 2. The ion had a multiplicity of 3. Two other geometries were also stable. Both resembled distorted doubly face-capped trigonal bipyramid geometries and lay considerably higher in energy (0.8 and 1.2 eV). Both had ground-state multiplicities of 2.

The most stable trimer, tetramer, and pentamer geometries were reoptimized with the nonlocal potential, which led to a breaking of the symmetry and changes in the bond lengths of several hundredths of an angstrom. The isosceles triangle lost all symmetry, the bond lengths being 2.32, 2.43, 2.28 Å. The ideal tetrahedron expanded and distorted, the side lengths being 2.49, 2.51, 2.51, 2.52, 2.53, and 2.58 Å (cf. 2.47 Å at the local level). The trigonal bipyramid also lost all symmetry, with the equatorial bonds being of lengths 2.65, 2.72, and 2.74 Å and the polar-equatorial bonds being of lengths 2.41 to 2.46 Å. In each case the ground-state multiplicity was not affected by the use of the nonlocal potential. The binding energies were reduced by many tenths of an electron volt, bringing them closer to the experimental values. The nonlocal calculations were considerably more expensive

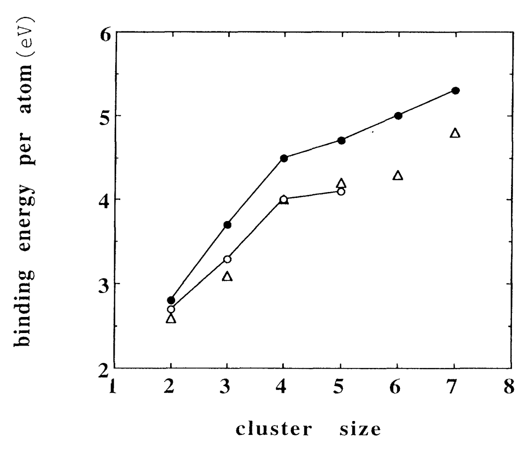

FIG. 2. Local (solid circles), nonlocal (open circles), and experimental [18] (open triangles) binding energies per atom (eV) for the most stable isomers. Experimental and nonlocal values for the tetramer coincide.

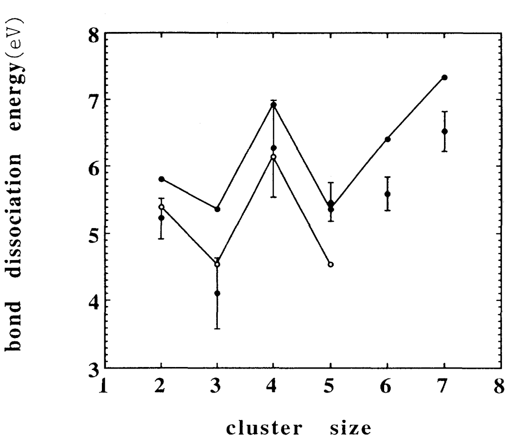

FIG. 3. Local (solid circles), nonlocal (open circles), and experimental [18] (solid circles with error bars) bond dissociation energies (eV) for the most stable isomers.

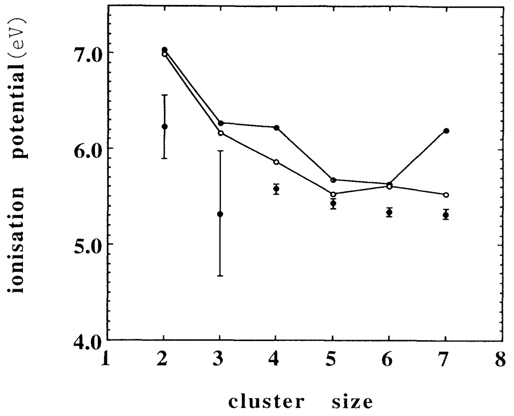

FIG. 4. Vertical (solid circles), adiabatic (open circles), and experimental [18] (solid circles with error bars) ionization potentials (eV) for the most stable isomers.

than the local ones. Thus we did not reoptimize the hexamer and the heptamer, although the trends are clear from the trimer, tetramer, and pentamer results. The calculated binding energies for the most stable geometries reproduce well experimental values [17,18], as shown in Fig. 2.

The binding energies of the most stable geometries, calculated with both local and nonlocal potentials, are seen to reproduce well the trends in the experimental data [17,18] (see Fig. 2). In this figure the binding energies are calculated with respect to free atoms. The overbinding of the local-density approximation is clear from the figure, with the nonlocal potential giving a marked improvement.

The bond dissociation energies are also in reasonable agreement with the experimental data [17,18] (see Fig. 3), although the experimental error bars are rather large. The bond dissociation energy was defined as the binding energy relative to the most stable cluster, with one atom less, and is thus the energy for loss of one atom. Loss of larger fragments was always more costly. The poor agreement for the pentamer suggests that we did not locate the lowest-energy geometry, or that our model incorrectly describes dissociation (for example, an intermediate energy barrier would account for the discrepancy).

The adiabatic ionization potentials for the most stable geometries are in reasonable agreement with experiment [17–21] (see Fig. 4), with the vertical potentials demonstrating the importance of relaxation that can account for changes in the energy of up to half an electron volt and changes in the bond lengths of several hundredths of an angstrom. Overall, the calculations overestimate the binding of the electron.

In summary we have used a *state-of-the-art* theoretical technique and extensive geometry optimizations to locate the preferred stable geometries for niobium clusters extending up to the heptamer. In general, the most stable geometries are compact and highly coordinated. An example is the pentagonal bipyramidal geometry favored by the heptamer. The less favorable geometries lie typically 1 eV higher in energy. Experiments have analyzed cold clusters that correspond to the most energetically favorable geometries. The experimental trends in the binding energies, the bond dissociation energies, and the ionization potentials are well reproduced by our calculations. However, the pentamer bond dissociation energy is smaller than expected, which leads us to suggest the presence of a more stable geometry or an intermediate energy barrier to dissociation. The ionic calculations demonstrate the importance of relaxation, with energy changes of half an electron volt in one case and bond length changes of several hundredths of an angstrom. The calculations with the nonlocal potential for the dimer to the pentamer led to no qualitative changes apart from a marked correction for the overbinding of the local potential.

These calculations demonstrate that transition-metal clusters can be studied with accurate theoretical methods, with a level of agreement with experiment comparable to that seen for the lighter elements. The stable structures should be useful to the development of semiempirical models for niobium and other transition elements.

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