An investigation into the physical, chemical and thermochemical properties of Niobium nanoclusters.

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Abstract

The search for spin-polarized metal clusters, energetic crystals and conductive materials is a paramount part of Nanotechnology. Adapting quantum chemistry and quantum mechanics methods to study and endeavor the electronic and lattice properties of groups of atoms in nanoclusters is a central approach, which aids in revealing crucial electronic properties that serve to develop and synthesize nanomaterials, nanometals and metal clusters. This project investigates the energy landscape of Niobium clusters (Nb_n), in order to shed light on their electronic, dipole, and magnetic properties. The clusters are studied with the XTB Tight-binding software coupled with hybrid DFT functionals. The results show that Niobium clusters in nanosized particles (10-61 atoms) bear ultra-low orbital gaps, with promising properties for hyperconnects and nanoparticle based electronics.

Introduction

Niobium (Nb) is a superconductor element [1] and is used for a range of various metallurgic purposes such as aerospace engineering, space programs and also in thermoresistant applications [2]. Novel innovations include the application of Nb-composites as interface stabilizers for high-temperature applications, given its high stability towards oxidizing conditions [3], while other applications include nanoelectronic devices applied for memory and data-storage purposes composed of Nb_2O_5 [4].

In this project, an investigation is made into the energy landscapes, physical and thermochemical properties of different Niobium crystals, encompassing several geometries in their neutral states. The size and geometries of the clusters is expected to give crucial insights into the distribution of electrons, the electronic properties and magnetic and electric characteristics. The results herein are important to develop new technologies based on the use transition metals as small particles, as also components in quantum computing devices.

Materials and Methods

Niobium crystals were build with the Amsterdam Density Functional suite [5] by constructing a *bcc* lattice of Niobium of dimensions 7x7x7 Å. The central atom was pinpointed, and the surrounding atoms in a radius of 6 Å were selected. This generated the source crystal, composed of 61 atoms, from which all substructures where generated. Atoms were removed in a symmetric manner, generating the configurations shown in Figure 1. All large geometries were assigned neutral charges, as only neutral species are studied in this work. This generated a total of X Niobium input configurations which were optimized geometrically using Grimme's tight-binding XTB program v. 5.6.4SE [6].

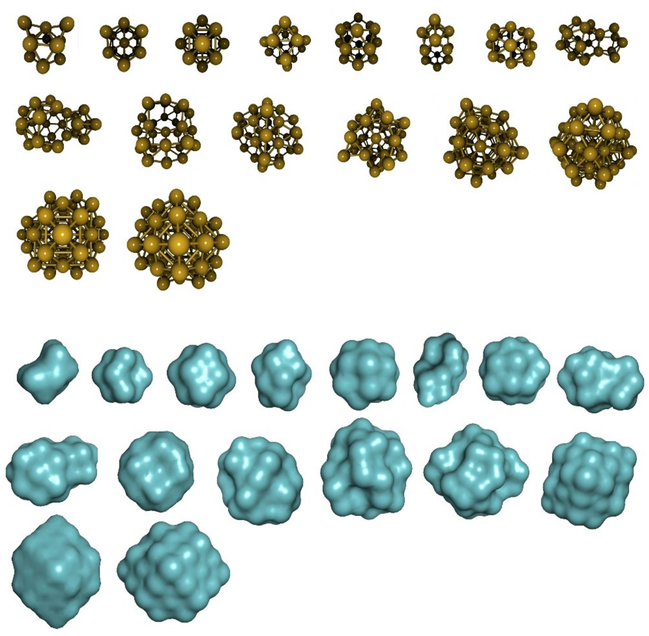

Figure 1. The converged Niobium nanocluster structures. From left to right in sequential order; Nb_{11}, Nb_{13}, Nb_{15}, Nb_{17}, Nb_{19}, Nb_{21}, Nb_{23}, Nb_{25}, Nb_{27}, Nb_{29}, Nb_{37}, Nb_{49}, Nb_{53}, Nb_{57}, Nb_{59}, Nb_{61}. Top half: Ball and stick models generated in Molden [7]. Lower half: Surface models generated in Pymol [8].

Results

The XTB tight-binding procedure gave a surprisingly fast conversion of the *bcc* nanoclusters to optimized forms (Fig 1). The set of the studied clusters ranged from 11 Niobium atoms to 61 atoms, and all clusters prepared in ADF [5] resulted in a total of 8 different symmetry groups (Table 1). The bond lengths in the small set of clusters (Nb_{11} – Nb_{17}) averaged a distance between Nb atoms of 2.72-3.3 Å. The Nb_{17} cluster assumed a structure with a large spherical hollow space in the interior, forming a hollow metal-spheres composed of a network of Niobium atoms with penta-coordinated states, and a few forming only four bonds (Fig 2). The same bond-length interval was observed for the medium-sized nanoclusters (Nb_{19}-Nb_{25} , Fig 3), however Nb_{19} was optimized to form a spherical metal nanocage, with a large hollow internal vacuum space. Similar shapes were observed for Nb_{21} and Nb_{25}.

The remaining clusters, the large set (Fig 4) contains four members of Nb nanoclusters with preserved C_{2h} geometries, (*bcc*) except the Nb_{53} cluster that displays a D_{3d} geometry. The bond lengths are respectively preserved in the interval 2.67-3.28Å for all the major clusters, and the clusters pertain the *bcc* geometry in their inner core. The electronic properties differ considerably, and are shown in Table 1

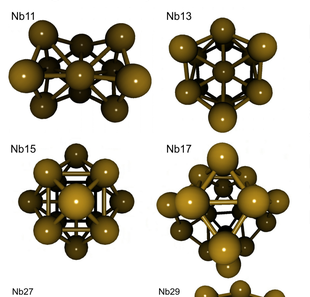

Figure 2. The optimized nanocluster geometries of the small set: Nb11-Nb17. Respective symmetries: C_{2v}, D_{3d}, O_h, C_2.

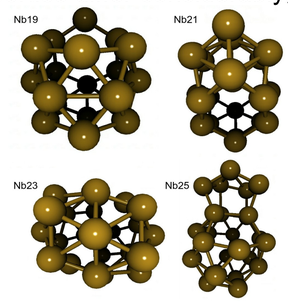

Figure 3. The optimized nanocluster geometries of the medium nanocluster set: Nb19-Nb25. Respective symmetries: C_s, C_s, C_2, C_1.

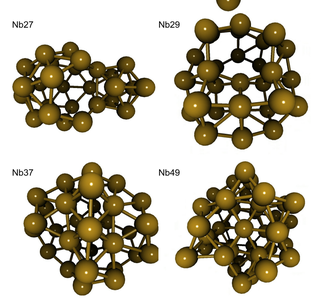

Figure 4. The optimized nanocluster geometries of the medium-large nanocluster set: Nb53-Nb61. Respective symmetries: D_{3d}, C_{2h}, C_{2h}, C_{2h}.a

Table 1. Electronic and thermochemical properties for Niobium nanoclusters. Symmetries derived with MOPAC [9]. Thermochemical properties derived with XTB [6]. G-tensor average between revTPSS [10] and M06-L method [11], calculated in ORCA [12]. Orbital gaps derived from M06-L calculations (where convergence is reached). Other electronic properties averaged between revTPSS and M06-L methods . Atomization energy derived using XTB. Abbreviation: N.C., Not Converged.

Cluster	Symmetry	XTB energy (Ht)	revTPSS Energy (Ht)	M06-L Energy (Ht)	ΔH_f (kcal/mol)	C(t) (cal/K/mol)	S (cal/K/mol)	Dipole (Debye)	Isotropic quadrupole	Orbital gap (eV)	Atomization energy (Ht)	G-tensor
Nb11	C_{2v}	-22.16	-625.95	-626.68	13.53	58.99	159.97	1.43	−177.84	0.39	3.55	2.00
Nb13	D_{3d}	-26.37	-739.91	-740.83	16.07	70.66	176.52	0.27	-207.94	0.56	4.21	2.00
Nb15	O_h	-30.37	-854.20	-855.16	18.50	85.05	190.95	0.04	-242.19	0.51	4.86	2.02
Nb17	C_2	-34.36	-967.35	-968.44	21.63	93.72	223.83	0.89	-270.97	0.33	5.66	1.99
Nb19	C_s	-38.67	-1081.30	-1082.50	24.20	105.13	242.96	0.43	-301.87	0.23	6.36	2.00
Nb21	C_s	-42.73	-1194.44	-1196.77	26.61	116.71	260.20	1.21	-334.94	0.18	6.93	2.00
Nb23	C_2	-46.71	-1309.53	-1311.02	29.40	128.30	280.95	1.59	−369,34	0.14	7.68	2.00
Nb25	C_1	-50.87	-1422.98	-1424.58	32.24	139.69	303.72	0.90	-391.40	0.19	8.31	2.00
Nb27	C_1	-54.95	-1537.09	-1538.81	34.76	151.18	322.51	1.95	-424.65	0.12	8.97	2.00
Nb29	C_2	-58.94	-1650.51	-1652.39	36.71	163.13	349.89	0.27	-455.85	0.15	9.67	2.00
Nb37	C_i	-75.26	-2106.36	N.C.	49.16	209.68	432.05	0.98	-583.29	0.11	12.37	2.00
Nb49	C_i	-99.63	N.C.	N.C.	65.68	279.12	557.43	N.C.	N.C.	N.C.	16.36	2.00
Nb53	D_{3d}	-107.79	N.C.	N.C.	71.02	302.25	594.41	N.C.	N.C.	N.C.	17.78	2.00
Nb57	C_{2h}	-115.95	N.C.	-3251.23	75.73	325.75	626.14	0.36	-967.72	0.00	19.02	2.00
Nb59	C_{2h}	-120.06	N.C.	N.C.	78.01	337.16	642.56	N.C.	N.C.	N.C.	19.72	2.00
Nb61	C_{2h}	-124.17	N.C.	N.C.	81.09	349.16	665.50	N.C.	N.C.	N.C.	20.43	2.00

Conclusions

The current results show that Niobium atoms may assemble in spherical hollow cages when the number of atoms is between 20 and 30. These nanoclusters have, by the use of the above given methods of calculation, the lowest orbital gaps, which are close to 0 eV. The larger clusters are not as facile to optimize with the XTB software, however, for $Nb_{57,}$ the structure appears as bulk material fragment, with has resulting 0 eV orbital gap. The composition of the large clusters prohibits a sound optimization of the structures with the XTB software, which although the particular symmetries are preserved, yields non-convergence in the quantum chemical calculations.

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