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Local bond-electron-energy relaxation of Mo atomic clusters and solid skins

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Abstract

A combination of the tight-binding theory, bond order-length-strength correlation and nonbonding-electron polarization notion, photoelectron spectrometrics, and density functional theory calculations has enabled us to examine the effect of atomic undercoordination on the local bond-electron-energy relaxation pertaining to Mo(100, 110) skins and atomic clusters. This exercise has led to the following quantitative information: (i) the atomic Mo 3d5/2 energy level located at 224.862 ± 0.004 eV shifts 2.707 eV deeper upon bulk formation; (ii) skin local bond is subject to 9.80% contraction; (iii) 5.952 e charge transfers from the inner to the outermost skin layer. Furthermore, the E4s level shifts from 61.229 eV for the Mo59 to 61.620 eV for the Mo15 cluster and the valence band undergoes a 1.057 eV upward shift. The globally positive core-level shift arises from the local quantum entrapment due to bond contraction and strength gain. The densely entrapped core electrons polarize the valence electrons and hence raise the valence band energy.

Keywords: Mo nanoclusters, XPS, DFT, BOLS, core level shift
1. Introduction

Solid skins and atomic clusters have attracted much attention both experimentally and theoretically due to their fascinating chemical and physical properties being different from their bulk counterparts. These abnormal properties include the dilute magnetism, catalytic ability, creation of Dirac-Fermions for topological insulators. All these properties are closely related to atomic undercoordination induced bond relaxation and electronic structure configuration. Therefore, exploring local electronic properties of systems induced by coordination imperfection would be crucial to improving the understanding of their electronic structure-related properties at the atomic level, such as cohesive energies, segregation energies, heats of mixing, and charge transferring.

Molybdenum (Mo) nanoclusters form a kind of interesting material used as media in ultrahigh density magnetic recording and as catalyst in various chemical processes, such as CVD growth of carbon nanotubes. Considerable effort has been made on the X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) investigation of the undercoordinated Mo systems. For example, Lundgren et al. found that the 3d core-level binding energy of the Mo(110) surface atom is lower by 333±10 meV relative to that of the bulk atoms using XPS. Yakovkin calculated the relaxation of the Mo(111, 112) skins and observed that the surface interlayer contracts by 16.5% and 13.4% in sequence, which is associated with the density redistribution and transformation of the electronic surface states. However, the measured core-level binding energy spectrum represents the mixture of the bulk component and the skin sublayers and the laws governing the energetic behavior of electrons and the electronic properties change of materials for the solid skins and atomic clusters remain unclear. It has been a great challenge to obtain quantitative information regarding the coordination-resolved surface relaxation, binding energy, and the energetic behavior of electrons localized in the solid skins and atomic clusters. Therefore, it is necessary to clarify the contribution of surface local relaxation and reveal the mechanism of the effects of coordination imperfection on the electronic
structure of skins and nanoclusters, which should be useful to understand their electronic structure-related properties at the atomic level.

In this work, we present our examination of the atomic under-coordination effect on the local bond relaxation, binding energy and the associated core-level energy shifts and valence band variation of Mo solid skins and atomic clusters based on bond order-length-strength (BOLS) correlation and nonbonding electron polarization (NEP) premise. Consistency between quantum calculations and photoelectron spectroscopy measurements of Mo skins and nanoclusters confirms our expectations that atomic undercoordination shortens and strengthens the bond, localizes and entraps core electrons, and polarizes the valence charge, which modified the Hamiltonian, atomic cohesive energy, local binding energy density and finally resulted in the unusual properties of Mo skins and nanoclusters.

2. Principles and calculation methods

2.1 BOLS-TB notation

According to the bond order-length-strength (BOLS) correlation, the shorter and stronger bonds between under-coordinated atoms result in local densification and quantum entrapment of the core electrons, which makes the valence charges polarize. The bond length and bond strength between under-coordinated atoms are closely associated with the effective atomic coordination number (CN), which is expressed as:

$$C_i = d_i / d_b = 2 \left\{ \left[ 1 + \exp \left( \frac{(12 - z_i)}{8z_i} \right) \right] \right\}$$

$$E_i = C_i^{-m} E_b$$

$$E_c(z) = z_i E_i$$

(1)

where $C_i$ is the coefficient of bond contraction with $z_i$ being the CN of an atom in the $i$th atomic layer, $i$ counts from the outermost atomic layer inward up to the third layer, $d_i$ and $E_i$ are the bond length and bond energy in the $i$th atomic layer, respectively, $E_c(z)$ is the atomic cohesive energy. The bond nature indicator $m$ represents how the bond energy changes with bond length. For most metals, $m = 1$. For nanoclusters, $z_i =$
4(1-0.75/K), \( z_2 = z_1 + 2 \) and \( z_3 = 12 \), where \( K \) represents the dimensional size equaling to \( R/d_b \). \( R \) is the real size of the specimen and \( d_b \) is the bulk bond length of the corresponding material.

According to the combination of BOLS correlation and the tight-binding theory\textsuperscript{21}, the single-body Hamiltonian is perturbed by the shorter and stronger bonds, denoted with \( \Delta_H \):

\[
H(\Delta_H) = -\frac{\hbar^2\nabla^2}{2m} + V_{\text{atom}}(r) + V_{\text{crys}}(r)(1 + \Delta_H),
\]

(2)

where,

\[
\Delta_H = \begin{cases} C_i^{\text{m} - 1} - 1 & \text{(Surface)} \\ \tau K^{-1} \sum_{i\leq 3} C_i(C_i^{\text{m} - 1}) & \text{(Nanocluster)} \end{cases}
\]

(3)

Note that, the shape factor \( \tau = 1, 2, \) and 3 corresponds to a thin plate, a cylindrical rod, and a sphere dot, respectively.

Regarding to the core level energies of a material, we mainly focus on two characteristic energies: the \( \nu \)th energy level of an isolated atom \( E_{\nu}(0) \) and the bulk shift (BS) \( \Delta E_{\nu}(12) = E_{\nu}(12) - E_{\nu}(0) \), where \( z = 12 \) means the bulk counterpart. The former is the integral of the eigen wave function and the intra-atomic potential, and the latter is its energy shift upon bulk solid formation. Both \( E_{\nu}(0) \) and \( \Delta E_{\nu}(12) \) for the particular \( \nu \)th band are intrinsic constant, disregarding the coordination and chemical environment of a given material, which follow the expressions:

\[
\begin{align*}
E_{\nu}(0) &= \langle \phi_{\nu}(r)|V_{\text{atom}}(r)|\phi_{\nu}(r) \rangle \quad \text{(Core level energy)} \\
\Delta E_{\nu}(12) &= \beta + z\gamma \propto \langle E_b \rangle \quad \text{(Core level shift)} \\
\beta &= \langle \phi_{\nu}(r)|V_{\text{crys}}(r)|\phi_{\nu}(r) \rangle \propto \langle E_b \rangle \quad \text{(Exchange integral)} \\
\gamma &= \langle \phi_{\nu}(r)|V_{\text{crys}}(r)|\phi_{\nu}(r') \rangle \propto \langle E_b \rangle \quad \text{(Overlap integral)}
\end{align*}
\]

(4)
where, $\phi_\nu(r)(r \neq r')$ is the Bloch wave function at a specific sites $r$. $z = 0$ and 12 represents an isolated atom and an atom in the ideal bulk, respectively. The exchange and overlap integrals are relative to the cohesive energy per bond $<E_b>$. Any perturbation to $\beta$ and $\gamma$ causes the shifts of energy level, so the core level energy shifts depend on the bond energy.

With respect to $\Delta E_\nu(12)$, the under-coordination induced the core level shift $\Delta E_\nu(z)$ for surface follows\textsuperscript{32}:

$$\frac{\Delta E_\nu(z)}{\Delta E_\nu(12)} = \frac{E_\nu(z) - E_\nu(0)}{E_\nu(12) - E_\nu(0)} = \frac{E_\nu}{E_b} = C_{z}^{-m} = 1 + \Delta H$$

or

$$\frac{E_\nu(z) - E_\nu(B)}{E_\nu(z') - E_\nu(B)} = \frac{C_{z'}^{-m} - 1}{C_{z}^{-m} - 1} \quad (z' \neq z)$$

(5)

With the given surface XPS spectral, we can determine the $z$-dependent $\nu$th energy of an isolated atom $E_\nu(0)$ and its BS ($\Delta E_\nu(12)$) by decomposing the spectral into surface components and bulk component with different-coordination number with the relations derived from Eq. (5):

$$\begin{cases}
E_\nu(0) = \frac{C_z E_\nu(z') - C_z E_\nu(z)}{C_{z'} - C_z} \\ 
\Delta E_\nu(12) = E_\nu(12) - E_\nu(0)
\end{cases} \quad (z' \neq z)$$

(6)

Similarly, incorporating the BOLS into the tight-binding theory yields the $\nu$th energy level shifts of nanocluster $\Delta E_\nu(K)$ as follows:

$$\Delta E_\nu(K) = E_\nu(K) - E_\nu(0) = \Delta E_\nu(12) + \Delta E_\nu(12)\Delta H \quad \text{or} \quad E_\nu(K) = E_\nu(12) + \Delta E_\nu(12)\Delta H,$$

(7)
where $E_v(K)$ is the XPS peak of the $v$th energy level of nanocluster. If a cluster is approximately spherical, the relationship of its size and atomic numbers ($N$) is $K^{1} = (3N/4\pi)^{1/3} \approx 1.61N^{1/3,23}$ thus, the $N$-dependence of core-level binding energy $E_v(N)$ can be derived from Eq. (3) and Eq. (7):

$$E_v(N) = E_v(12) + 1.61\pi \Delta E_v(12) \sum_{i \leq 3} C_i (C_i^{-m} - 1) N^{-1/3}$$

(8)

Generally, the size-induced BE shifts for nanoclusters depends inversely on the size in the form of, $E_v(K) = A + B K^{-1}$, where $A$ and $B$ are constants that can be determined by finding the intercept and the slope of the $E_v(K)$ line, respectively. According to the relationship of $K$ and $N$, we can deduce the form of $N$ versus BE shift into $E_v(N) = A + 1.61BN^{-1/3} = A + B' N^{1/3}. Comparing the experimental scaling relationship with the theoretical expression yields,
Using Eq. (6) or (11), we can readily determine the energy level $E_v(0)$ of an isolated atom and its BS $\Delta E_v(12)$ by analyzing the measurements. Note that, for the same element, the $E_v(0)$ and $E_v(12)$ are intrinsic constants for all surfaces, disregarding the coordination and chemical environment of a given material.

For the detectable quantities can be directly connected to the bond identities such as bond nature, order, length and strength, we are able to predict coordination number resolved the local bond strain ($\epsilon(z)$), relative binding energy density($\delta E_D$), relative core-level binding energy shift ($\delta E_c$), and the relative cohesive energy per atom ($\delta E_C$) in the surface skins,

\[
\begin{align*}
\epsilon(z) &= C_z - 1 (\%) \\
\delta E_D &= E_D(z) / E_D(12) - 1 = C_z^{-4} - 1 (\%)
\end{align*}
\]

\[
\begin{align*}
\delta E_c &= \Delta E_v(z) / \Delta E_v(12) - 1 = C_z^{-m} - 1 (\%)
\end{align*}
\]

\[
\begin{align*}
\delta E_C &= E_C(z) / E_C(12) - 1 = z_{ib} C_z^{-m} - 1 (\%)
\end{align*}
\]

(12)

with $z_{ib} = z_i / 12$. Subscript $i$ denote the atomic layers counted from the outermost inwards. These basic quantities determine the related properties at the specific atomic site. For instance, atomic cohesive energy dominates the critical temperature of melting$^{24-26}$ and the binding energy density determines the elastic modulus$^{27,28}$.

### 2.2 DFT calculations

In order to verify the BOLS predictions on the coordination imperfection induced the core-level entrapment and the valence charge polarization, we conducted DFT calculations on the optimal bond relaxation, charge transfer$^{29}$, and the energetic distribution of the core band and valence states of Mo nanoclusters with different
structures\textsuperscript{30,31}, as shown in Fig. 1. Moreover, we also compared the computational results with the photoelectron spectroscopy measurements.

The DFT calculations were performed using the DMol3 code with a double numeric plus polarization basis set\textsuperscript{32}. During the DFT calculations, the potentials of core electrons were assumed to be DFT semi-core pseudopotential\textsuperscript{33}. The DFT exchange-correlation potential utilized the local-density approximation (LDA), with the PWC function for geometry and electronic structures\textsuperscript{23,34}. PWC is the default functional for DMol3 calculations. The self-consistency threshold of total energy was set at $10^{-6}$ au in calculations. The tolerance limit for the energy, forces, and displacement in geometry optimization were taken at $10^{-5}$ Hartree, 0.002 Hartree/Å, and 0.005 Å, respectively.

3. Results and Discussion

3.1 Surface core level quantum entrapment

To better understand the effects of coordination imperfection and the physical origin of surface core level shift, we decomposed the Mo 3$d_{5/2}$ spectra of the clean surface Mo(100) and Mo(110) in Fig. 2\textsuperscript{12,35}. Obeying the constraints given in Eq.(5), the spectra from clean surface of Mo(100) and Mo(110) specimen were decomposed with three components, corresponding to the bulk (B), surface skins $S_2$ and $S_1$ from higher (smaller absolute value) to lower BE after the subtraction of the Tougaard background\textsuperscript{36}. Table 1 summarizes the optimal component energies, the corresponding $z_i$, and the $z$-resolved local bond strain ($\varepsilon_z$), the relative binding energy density ($\delta E_D$), the relative core-level binding energy shift ($\delta E_z$), and the relative cohesive energy per atom ($\delta E_C$) were summarized.

From the decomposition, we obtained the $E_{3d_{5/2}}(0)$, $\Delta E_{3d_{5/2}}(z)$ and the standard deviation ($\sigma$) by using a least root-mean-square method. A fine-tuning of the CN values of the components will minimize $\sigma$ and improve the accuracy of the effective CN for each sublayer. It has been derived that the $3d_{5/2}$ BE of bulk and surface skin shift deeper from 2.707 to 3.100 eV with respect to that of the isolated Mo (224.862 ±
0.004 eV) atoms. The following describes the obtained the \( z \)-resolved \( 3d_{5/2} \) BE shift for Mo skins:

\[
E_{3d_{5/2}}(C_z) = \langle E_{3d_{5/2}}(0) \rangle \pm \Delta E_{3d_{5/2}}(B) C_{z}^{-m} = 224.862 \pm 0.004 + 2.707 C_{z}^{-1}
\]

These refinement led to the effective atomic CNs of the top (second) Mo (100, 110) atomic layers as 3.98 (5.16) and 3.95 (5.83). With the derived \( z \) value and the \( 3d_{5/2} \) BE for each XPS component, we could predict the \( z \)-resolved local bond strain \( \varepsilon_z(z) \), the relative BE shift \( \delta E_z(z) \), the relative atomic cohesive energy \( \delta E_c(z) \) and the relative binding energy density \( \delta E_D(z) \) of the Mo surface skins, as shown in Fig. 3. It is found that the undercoordination-induced local bond strain contracted, relative binding energy density enhanced, relative atomic cohesive energy weakened and relative core-level binding energy shifted positively up to 12.67\%, 71.92\%, 62.31\%, 14.51\%, respectively, for the outermost three atomic layer of Mo surface. The fundamental information we have derived is of great importance in determining the surface properties and surface processes.

### 3.2 Bond contraction, core level entrapment and valence charge polarization

According to the BOLS-NEP, bonds between under-coordinated atoms in low-dimensional system are shorter and stronger, which makes the potential well deeper and hence the core-level energy levels of these atoms drop correspondingly. Polarization induced by the densely trapped bonding electrons will take place if nonbonding electrons exist. To further confirm our predictions, we performed the bond contraction, binding energy and valence local DOS of Mo\(_N\) clusters described by Finnis–Sinclair potentials\(^{30}\) with different size and structure from the perspective of DFT calculations, as shown in Fig.1. From the DFT results of the bond length and bond contraction between atoms of Mo\(_N\) clusters, we can find that atoms in the cluster interior have no contraction equaling to the ideal distance of the corresponding bulk atom, while the skin atoms with under-coordinated number contract, which was listed in Table 2. And the smaller the CN is, the stronger the bond contracts, that is, the extent of these clusters skin atoms contraction depends on its CN. The results agree well with the reported bond contraction of Ag, Au, Cu, Ni, Pd, Pt, Fe atomic chains\(^{37}\).
We also estimated the charge flow of these Mo nanoclusters using the Mulliken population analysis and found that the electrons flowed from the inner to the outermost layer of the clusters, which were also listed in Table 2. The negative sign represents charge loss. It indicated that the interaction between under-coordinated atoms induced quantum entrapment, and hence resulted in the core electron entrapment from the local sites and the densification of charge and energy.

Fig. 4 showed the 4s BE (a) and LDOS (b) for the C$_{2v}$, C$_{2v}$, D$_{5v}$, C$_{2v}$, C$_{5v}$, C$_{2v}$, and O$_{h}$ structures calculated by DFT. It is readily shown that the 4s level shifts from 61.229 eV for the Mo$_{59}$ nanocluster to 61.620 eV for the Mo$_{15}$ nanocluster while the LDOS peak shifts from -0.897 eV for Mo$_{59}$ to 0.160 eV for Mo$_{15}$. This illustrates that both the core-level atoms localization-entrainment and the valence charge polarization take place in these Mo nanoclusters, and hence lead to positive core level shift and negative valence band shift. Both of them exhibit stronger bonds with the size decreasing. These DFT calculations further confirmed our BOLS-NEP predictions.

### 3.3 N-resolved $E_4s(N)$

Choosing Mo$_{59}$ cluster for the standard reference, we can obtain its dimensional size $K = R/d_b = 1.714$, for $R$ is 4.672 Å and the $d_b$ is 2.725 Å of Mo$_{59}$. According to Eq. (1), we can estimate $z_1 = 4(1-0.75/K) = 2.25$ and $z_2 = z_1+2 = 4.25$ and thus obtain $C_1$ and $C_2$ being 0.7356 and 0.8865, respectively. Fig.5 shows that $E_{4s}(N)$ of Mo nanoclusters depends linearly on $N^{-1/3}$, which gives the y-intercept and the slope are 60.760 and 2.062, respectively. According to the y-intercept and slope derived from $N$-induced Mo $E_{4s}(N)$ and Eq. (11), we can obtain:

$$E_{4s}(12) = 60.760 \text{eV and } \Delta E_{4s}(12) = 3.389/\tau$$

Because the shape of Mo nanocluster is not an ideal sphere, the shape factor $\tau$ is uncertain, which should be greater than unity and smaller than three. Although the bulk shift of Mo $\Delta E_{4s}(12)$ is absent, we have obtained the $\Delta E_{3d5/2}(12) = 2.707 \text{ eV}$. Though the shifts of different core level energy have a slight deviation, but the core level band of nanoclusters shifts down as a whole, so we assume the BS shift of $E_{4s}$
and $E_{3d_{5/2}}$ the same to obtain the information of $E_{4s}$. Therefore, we can determine the value of $\tau$ being 1.252. Thus, $N$-resolved $E_{4s}(N)$ follows:

$$E_{4s}(N) = E_{4s}(12) + 1.61\tau \Delta E_{4s}(12) \sum_{i \leq 3} C_i (C_i^{-m} - 1) N^{-1/3} = 60.760 + 2.062 N^{-1/3}$$

Such a consistency of DFT calculations and BOLS predictions evidences that the local bond contraction and quantum entrapment will lead to a densification of mass, charge and energy near the undercoordinated atomic site, which resulted in the enhancement of the Hamiltonian and hence the positive BE shifts for Mo skins and nanoclusters. Therefore, the interaction between undercoordinated atoms dominates the behavior of BE shifts.

4. Conclusion

Consistency between DFT calculations and photoelectron spectroscopy measurements confirmed our BOLS-NEP predictions of the atomic CN effects on the local bond relaxation, electron binding-energy shift, and valence charge transfer of Mo skins and nanoclusters. It was clarified that Mo $3d_{5/2}$ $(4s)$ shifts positively by 2.707 eV from a value of 224.862 (58.053) eV for an isolated atom to 227.569 (60.760) eV for the bulk. The interaction between under-coordinated atoms caused local strain, local densification and entrapment of the core electrons, as well as valence charge polarization, which perturbed the Hamiltonian and hence dominated the unusual behaviour of Mo surfaces and nanoclusters. Findings will be useful to apply Mo skins and nanoclusters in practical application, such as catalytic enhancement, applications in electronics and optics.

Acknowledgment

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References

Table and Figure captions:

Figure 1 Global minima of Moₙ clusters described by Finnis–Sinclair potentials.

Figure 2 Decomposition of the Mo 3d₅/₂ spectra for (a) Mo(100) and (b) Mo(110) surfaces with three Gaussian components representing the bulk B, S₂, and S₁ components from higher(smaller absolute value) to lower BE, which obey the BOLS constraints given in Eq. (5). The related derived information is listed in Table 1.
Figure 3 CN-resolved (a) local bond contraction $\varepsilon_z(z)$, relative BE shift $\delta E_z(z)$, (b) relative atomic cohesive energy $\delta E_C(z)$ and relative binding energy density $\delta E_D(z)$.

Figure 4 Undercoordination induced (a) core-level energy level entrapment and (b) valence band polarization of Mo clusters ($C_{2v}^{15}$, $C_1^{18}$, $D_2^{20}$, $C_2^{28}$, $C_4^{47}$, $C_5^{51}$, $O_h^{59}$), indicating the extent of entrapment and polarization depends on the cluster size.

Figure 5 The $N$-resolved $E_{4s}$ of free Mo$_N$ nanoclusters.
Table 1: Atomic-layer and crystal-orientation resolved the effective CN(z), bond contraction ($\varepsilon_z$), relative BE shift ($\delta E_z$), relative atomic cohesive energy ($\delta E_C$), and the relative binding energy density ($\delta E_D$) determined from the measured XPS profiles of Mo (100) and (110) surfaces under the established approach and the criteria.

<table>
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<th>Structure</th>
<th>$i$</th>
<th>$E_{3d^5} (\text{eV})$</th>
<th>z</th>
<th>$-\varepsilon_z$</th>
<th>$\delta E_z$ (%)</th>
<th>$-\delta E_C$ (%)</th>
<th>$\delta E_D$ (%)</th>
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<td>Bulk</td>
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<td></td>
<td></td>
<td></td>
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<td>12.67</td>
<td>14.51</td>
<td>62.31</td>
<td>71.92</td>
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Table 2: DFT calculation results of the bond length ($d_i$), bond contraction coefficient ($C_z$), and charge transfer of Mo$_N$ clusters. The charge transfer (Mulliken population analysis) of different structures reveals charge flow from the inner to the outermost atomic shells due to the quantum entrapment.

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<tr>
<th>Structure</th>
<th>$d_{12} (\text{Å})$ (Atomposition 1-2)</th>
<th>$C_z-1$ (%) (Shell layer 1-2)</th>
<th>Charge Transfer (e)</th>
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<tr>
<td>O_{h}59</td>
<td>2.560</td>
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