Orbitalwise Coordination Number for Predicting Adsorption Properties of Metal Nanocatalysts

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We present the orbitalwise coordination number CN^{α} ($\alpha = s$ or d) as a reactivity descriptor for metal nanocatalysts. With the noble metal Au ($5d^{10}6s^{1}$) as a specific case, the CN^{s} computed using the two-center s-electron hopping integrals to neighboring atoms provides an accurate and robust description of the trends in CO and O adsorption energies on extended surfaces terminated with different facets and nanoparticles of varying size and shape, outperforming existing bond-counting methods. Importantly, the CN^{s} has a solid physiochemical basis via a direct connection to the moment characteristics of the projected density of states onto the s orbital of a Au adsorption site. Furthermore, the CN^{s} shows promise as a viable descriptor for predicting adsorption properties of Au alloy nanoparticles with size-dependent lattice strains and coinage metal ligands.

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Metal nanoparticles exhibit distinct physiochemical properties from their bulk counterparts. This phenomenon manifests itself in numerous applications such as chemical and biological sensing [1], targeted drug delivery [2], and heterogeneous catalysis [3]. Understanding effects of particle size, shape, and composition on the binding affinity of molecules to surface metal atoms is of key importance for rational design of functional materials with the utmost efficiency and durability. In recent years, many efforts have been made aiming to correlate the binding energies of an adsorbate on metal surfaces with the electronic or geometric factors of the adsorption site (termed descriptor) [4–11]. The moment characteristics of the projected density of states onto valence orbitals of a transition-metal atom, e.g., d-band center [4], have been successfully used as reactivity descriptors for planar transition-metal surfaces, while transferring the concept to nanometer-sized systems is problematic due to the discrete nature of electronic states and/or a formidable computational cost. Mpourmpakis *et al.* proposed a dual-descriptor model with the coordination number and curvature angle of surface metal atoms for capturing structural and reactivity properties of Au nanoclusters [9]. Recent work by Calle-Vallejo *et al.* introduced the generalized coordination number $\overline{\mathrm{CN}}$ as a single reactivity descriptor for Pt nanocatalysts that can be easily computed from the local atomic arrangement of an adsorption site [11–13]. Although both revised bond-counting methods beyond first nearest-neighbor atoms capture the general trend of adsorption properties of planar surfaces and shape-specific nanoparticles of pristine metals, their application to complex systems with varying lattice strains and metal ligands is out of reach due to the lack of an explicit consideration of interatomic interactions.

In this Letter, we propose the orbitalwise coordination number CN^{α} ($\alpha = s$ or d) as a reactivity descriptor for metal nanocatalysts. The CN^{α} quantifies the degree of coordinative saturation of metal atoms and their inclination to form new bonds via the α orbital of an adsorption site. In surface chemistry, the coordinative saturation is an often-used concept for understanding adsorption site preferences [14], trends of surface reactivity [15], and scaling relations among adsorption energies of hydrogen-containing species [16]. For example, hydrogenating an electronegative adatom A that initially adsorbs at a hollow site of a metal surface by creating an A–H bond will decrease its binding strength to surface atoms and likely shift the adsorbate to a less coordinated bridge or atop site, obeying the bond-order conservation principle [14,15,17]. In reverse thinking, saturating a surface metal atom by an introduction of extra neighbors of the same type or by a replacement with more reactive metal atoms will decrease its chemical reactivity towards adsorbing species. Intuitively, the variation in adsorbate binding energies across nonuniform sites of a metal surface is strongly dependent on the local coordination environment. Nevertheless, a rigorous definition of the coordination-based reactivity descriptor that is rooted on a solid theoretical basis and ambiguously distinguishes between inequivalent sites of metal nanocatalysts remains elusive.

To unravel intrinsic reactivity trends of metal nanocatalysts, we use a series of freestanding Au nanoparticles with varying size (diameters from ∼0.5 to ∼2 nm) and shape (cuboctahedron, truncated octahedron, tetrahedron, and cube) as model systems. The surface of metal nanoparticles studied here is composed of the {111} and {100} terrace atoms, and the step and kink atoms at the intersection of neighboring facets [18]. We first probe the chemical reactivity of individual surface atoms of Au metal nanoparticles with molecularly adsorbed carbon monoxide (CO) in a straight up configuration at the atop site. All adsorption energy calculations were performed on the basis of density functional theory (DFT) using generalized gradient approximations with the Perdew-Burke-Ernzerhof exchange-correlation functional (GGA-PBE) [19] and the projector augmented-wave method implemented in real-space GPAW [18,20,21]. Figure S1(a) [18] shows that the $\overline{\mathrm{CN}}$ of inequivalent surface Au atoms of truncated octahedral nanoparticles linearly correlates with CO adsorption energies ($R^2 = 0.90$), similar to previous studies on Pt nanocatalysts [11]. Here, the $\overline{\mathrm{CN}}_i$ is computed as a sum of the weighted metal-metal coordination $\mathrm{CN}_j/\mathrm{CN}_\infty$, where the CN_j represents the regular coordination number of the atom j, the index j goes through the first nearest neighbors of the surface atom i, and the normalization factor CN_∞ is 12 and 8 for fcc/hcp and bcc metals, respectively [11,12]. Nevertheless, the correlation coefficient (R^2) significantly degrades if different shapes of Au nanoparticles are also included in the regression ($R^2 = 0.75$), see Fig. 1(a). Extending the $\overline{\mathrm{CN}}$ to further neighbors only slightly improves its correlation with CO binding energies, see Fig. S1(b) [18].

To go beyond the simple bond-counting scheme and explicitly consider interatomic interactions in defining the local coordination, we are in search of pair-additive physical factors that quantify the influence of neighboring atoms on the chemical reactivity of an adsorption site. In light of the importance of the electronic structure of surface metal atoms in determining the nature and strength of chemical bonding, we resort to moment characteristics of the projected density of states onto the transition or noble metal atom i with a given eigenspectrum $\{\varepsilon_i^\alpha\}$ ($\alpha = s$ or d) and aim to unearth their connection to the coordination environment. From the moments theorem [22], the zeroth and first moments ($M_{0,i}^\alpha$ and $M_{1,i}^\alpha$) of the distribution $\{\varepsilon_i^\alpha\}$ are the total number of atomic orbitals N_α and the average band energy ε_α (zero if it is set as the energy reference), respectively, thus giving no distinctive electronic structure information of surface atoms. Arguably, the second moment $M_{2,i}^\alpha$ characterizing the width of the distribution $\{\varepsilon_i^\alpha\}$ mainly governs the variation in the local chemical reactivity of an adsorption site perturbed by neighboring atoms. Within the linear combination of atomic orbital formalism [18,23,24], the second moment $M_{2,i}^\alpha$ of the projected density of states onto the α orbital at the site i is pair additive with respect to the square of two-center α-electron hopping integrals $(t_{ij}^{\alpha\beta})^2$ from the α orbital at the atom i to all β orbitals of the neighboring atom j within a cutoff radius r_c,

$$M_{2,i}^\alpha = \sum_j^{r_{ij}<r_c} \sum_\beta (t_{ij}^{\alpha\beta})^2 = \sum_j^{r_{ij}<r_c} \sum_\beta |\langle \psi_i^\alpha | \mathcal{H} | \psi_j^\beta \rangle|^2, \qquad (1)$$

where ψ_i^α and ψ_j^β are the wave functions of the α and β atomic orbitals at the site i and j, respectively, $\mathcal{H}$ is the one-electron Hückel Hamiltonian [25], and the summation j extends over all neighbors of the atom i within a cutoff radius r_c. The angular variation of hopping integrals between atomic orbitals as one atom is rotated around the other is quite complicated, and was tabulated by Slater and Koster [26]. Thanks to the invariance of object shape under translation and rotation, the second moment of the distribution $\{\varepsilon_i^\alpha\}$ can be directly computed using the α-electron hopping integral matrix $(t_{ij}^{\alpha\beta})$ where the two atoms are aligned along the z axis [18,24], see Table I. With the tight-binding approximation, the two-center α-electron hopping integrals depend on the orbital size or shape and internucleus distance, i.e., $t_{ij}^{ss} = \eta_{ss}\hbar^2/md_{ij}^2$, $t_{ij}^{sd} = \eta_{sd}\hbar^2 r_{d,j}^{3/2}/md_{ij}^{7/2}$, and $t_{ij}^{dd} = \eta_{dd}\hbar^2 r_{d,i}^{3/2} r_{d,j}^{3/2}/md_{ij}^5$, where the symmetry-dependent coefficient η and the spatial extent of the d orbital r_d of transition and noble metals are tabulated [27]. Rooted on the pair additivity of the second moment in Eq. (1), we introduce the orbitalwise coordination numbers CN^α ($\alpha = s$ or d) of the atom i, written as [18,23]

$$\mathrm{CN}_i^\alpha = \frac{M_{2,i}^\alpha}{(t_{nn}^{\alpha,\infty})^2}, \quad \text{where } \alpha = s \quad \text{or} \quad d, \qquad (2)$$

where $(t_{nn}^{\alpha,\infty})^2$ is a sum of the square of the α-electron hopping integrals to relevant valence orbitals of a first nearest-neighbor atom in the optimized bulk [18].

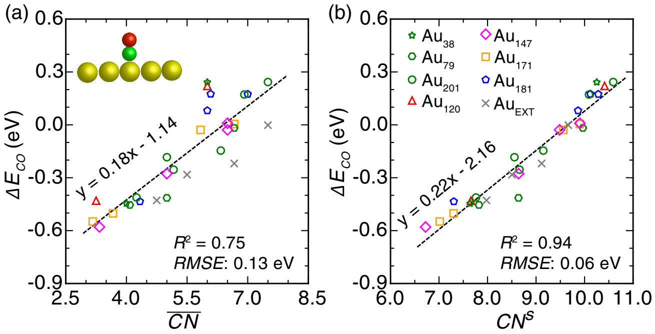

FIG. 1. Adsorption energies of the atop CO on Au nanoparticles and extended surfaces described by (a) the generalized coordination number $\overline{\mathrm{CN}}$ [11], and (b) the orbitalwise coordination number CN^s computed using the two-center s-electron hopping integrals. Linear regression lines (dashed) and related statistics are also given.

TABLE I. The α-electron hopping integral matrix $t_{ij}^{\alpha\beta}$ between the two atoms aligned along the z axis [24,27].

$t_{ij}^{\alpha\beta}$	s	d_{xy}	d_{yz}	d_{xz}	$d_{x^2-y^2}$	d_{z^2}
s	$ss\sigma$	0	0	0	0	$sd\sigma$
d_{xy}	0	$dd\delta$	0	0	0	0
d_{yz}	0	0	$dd\pi$	0	0	0
d_{xz}	0	0	0	$dd\pi$	0	0
$d_{x^2-y^2}$	0	0	0	0	$dd\delta$	0
d_{z^2}	$ds\sigma$	0	0	0	0	$dd\sigma$

With the minimal basis set in a linear combination of atomic orbital description of the electronic structure for Au ($5d^{10}6s^1$), we found that the CN^s of surface Au atoms of extended surfaces ({111}, {100}, {211}, and {532}) and nanoparticles (varying size and shape) computed using the two-center s-electron hopping integrals to neighboring s and d orbitals ($r_c = 5.5$ Å or equivalently up to second nearest neighbors) shows a strong linear correlation with the CO adsorption energies ($R^2 = 0.94$). As expected, if a surface Au atom becomes less (more) coordinated with its neighbors, i.e., the CN^s is smaller (larger), the CO adsorption would be stronger (weaker). The CN^d, obtained using the two-center d-electron hopping integrals to neighboring s and d orbitals [18], and the simple summation of the interatomic coupling matrix elements defined previously [6] still show a good linear correlation to CO adsorption energies because of the similar power-law dependence of s- and d-electron hopping integrals on the bond distance [27]. However, the d-state contribution to the surface chemical bonding is expected to be less important since the d orbitals of a Au atom are fully occupied and the d-band center is further down the Fermi level, see Fig. S2(a) [18]. Not surprisingly, the CN^d outperforms the CN^s for transition metals with partially filled d bands, such as Pt (to be discussed in a future publication). To simplify the argument, we will focus on the CN^s in the following analysis for Au. Considering the simplicity of the descriptor, the observed linear relationship shown in Fig. 1(b) is striking. Compared with the purely geometry-based $\overline{\mathrm{CN}}$ [11,12] as shown in Fig. 1(a), the model with the CN^s as a reactivity descriptor shows improved performance in terms of the correlation coefficient and statistical errors. If the bulk geometry of nanoparticles without relaxation is used for computing the CN^s, its correlation with CO adsorption energies decreases and becomes similar to that using the $\overline{\mathrm{CN}}$. Therefore, we attributed the improvement of the new reactivity descriptor CN^α over the $\overline{\mathrm{CN}}$ to the explicit consideration of lattice strains that are highly dependent on the size and shape of metal nanoparticles [28].

To unravel underlying electronic factors governing variations in the CN^s and thus further understand reactivity trends across surface Au atoms, we show in Fig. 2(a) the density of states projected onto the s orbital of the terrace, step, and kink atoms of the truncated octahedral Au_{201} nanoparticle. Clearly, as a surface Au atom becomes less coordinated with its neighbors, the width of the s band measured by the second moment $M_{2,i}^s$ decreases, which results in an upshift of the center of gravity of the occupied s-states ε_s^*. Since the cohesion of noble metal atoms is mainly determined by the interaction of valence s electrons with neighboring s and d electrons, the cohesive energies of surface Au atoms can be directly linked to the one-electron energy distribution of the s band with the aid of the moments theorem [22,24] and to the orbitalwise coordination number CN^s using the bond-cutting model [29,30]. The theoretical relation between ε_s^* and the CN^s can be written as [18]

$$\varepsilon_s^* = \varepsilon_s^{*,\infty} + \frac{E_{\mathrm{coh}}^{\infty}}{2\theta_s}\left(\frac{\mathrm{CN}^s}{\mathrm{CN}_{\infty}^s} - 1\right), \tag{3}$$

where $\varepsilon_s^{*,\infty}$ is the center of gravity of occupied s states projected onto a bulk atom, θ_s is the theoretical filling of the s band (0.5 for Au), and $E_{\mathrm{coh}}^{\infty}$ (negative sign convention) is the cohesive energy of a bulk atom. Using the DFT-calculated $\varepsilon_s^{*,\infty}$ (−5.3 eV), $E_{\mathrm{coh}}^{\infty}$ (−3.19 eV) of a Au atom in the fcc bulk, and the CN_{∞}^s (13.3), the theoretical line between ε_s^* and the CN^s is presented in Fig. 2(b). A linear regression of ε_s^* on CN^s is performed for inequivalent surface Au atoms of extended surfaces and nanoparticles, which shows an excellent agreement with the theoretical model. The observation shown in Fig. 2 sheds light on the electronic origin of the CN^s and provides a solid theoretical basis for using the orbitalwise coordination number CN^α as a reactivity descriptor for metal nanocatalysts.

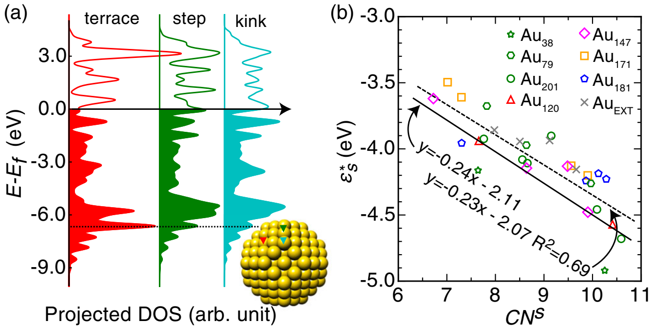

FIG. 2. (a) Density of states projected onto the s orbital of surface Au atoms on the terrace, step, and kink atoms of the Au_{201} nanoparticle, and (b) the relationship between ε_s^* and the CN^s for various surface atoms of extended Au surfaces and nanoparticles. The dashed line is the least-square fit; the sold line is the theoretical correlation, corresponding to Eq. (3).

The question that still remains to be answered is why there is a linear correlation between the coordination numbers (e.g., CN, $\overline{\mathrm{CN}}$, and CN^α) of a surface metal atom and its local chemical reactivity. This is often assumed based on intuition rather than rigorously proved. According to the bond-order conservation principle in chemisorption [14,15,17], the total bond order χ of a surface metal atom i, which is coordinated with its nearest neighbors and a covalently bonded adsorbate A at an atop site, for example, is conserved and normalized to unity along all surface metal atoms

$$\chi_{im} + \chi_{iA} = 1, \tag{4}$$

where χ_{im} and χ_{iA} are the bond order of the atom i with the surrounding metal atoms and with an adsorbate A,

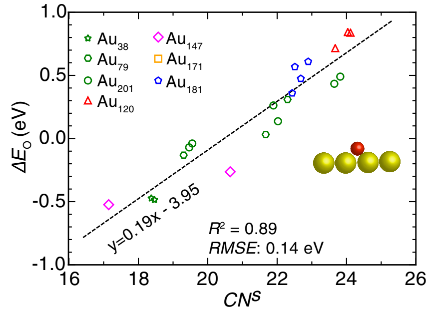

FIG. 3. Description of adsorption energies of atomic O on hollow sites of Au nanoparticles by the orbitalwise coordination number CN^s. Related statistics of the linear regression are shown.

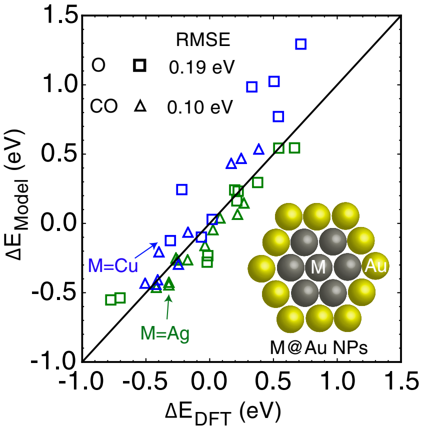

FIG. 4. The prediction of CO and O adsorption energies on a series of M@Au ($M = \text{Cu}$ or Ag) core-shell nanoparticles (38, 79, and 201 atoms) using the CN^s as a reactivity descriptor and theoretical relationships developed from pure Au nanocatalysts.

respectively. We argue that χ_{im} is not pair additive with respect to the coordination number CN, but rather has a weaker dependence, following $\chi_{im} \propto \sqrt{\text{CN}}$. This is in analogy to the square-root bond-cutting model for describing variations in the cohesive energies of surface metal atoms ($E^i_{\text{coh}} \propto \sqrt{\text{CN}_i}$) [31]. If the two-center interatomic potential of the adsorbate A with the metal atom i can be represented by a Morse-type potential, $\Delta E_A = -Q_0(2\chi_{iA} - \chi^2_{iA})$, where Q_0 is the equilibrium bond energy of the adsorbate A with an isolated atom i, the adsorption energy ΔE_A, to a first-order approximation without a consideration of the metal-metal and intra-adsorbate relaxations upon adsorption, is then linearly proportional to $\sqrt{\text{CN}}$, or more generally to $\sqrt{\overline{\text{CN}}}$ and $\sqrt{\text{CN}^\alpha}$.

Thanks to the generality of the bond-order conservation principle discussed above, the CN^s of the hollow sites comprised by multiple atoms (e.g., three atoms for 111-type hollow sites) should also reflect the trend of their intrinsic chemical reactivity to probing species. As a straightforward extension, the CN^s of a hollow Au site can be computed by a sum of the square of normalized s-electron hopping integrals to all neighbors within the cutoff radius r_c while explicitly excluding the atom-atom hopping within the adsorption site. With this definition, the CN^s of a fcc and hcp hollow site on Au$\{111\}$ is 23.4 and 23.8, respectively, which are larger than the coordination number (15 and 16) due to the broken-bond strains and long-range interactions explicitly considered in Eq. (2). We use the atomic O as the probing species for the reactivity of hollow sites on Au nanocatalysts. In Fig. 3, we showed the correlation between the CN^s of hollow sites of Au metal nanoparticles with adsorption energies of the atomic O. Compared with the $\overline{\text{CN}}$ (see Fig. S4) [18], the CN^s exhibits improved linear relationships with the local chemical reactivity of hollow sites ($R^2 = 0.89$).

The key advantage of the orbitalwise coordination number CN^α compared to the CN and $\overline{\text{CN}}$ as a reactivity descriptor is that it can be naturally extended to alloy systems. This extension is guaranteed in Eq. (2) since the electron hopping integrals are dependent not only on the geometric arrangement but also on the metal identity of an adsorption site. Given the linear relationships between the CN^s of a surface site i on pure Au nanocatalysts and the CO and O binding energies as shown in Figs. 1(b) and 3, respectively, we aim to predict the surface reactivity of Au alloy nanoparticles where the local coordination environment of Au surface atoms is fine-tuned by metal ligands. We chose Au core-shell alloy nanoparticles (Ag@Au and Cu@Au) as the test systems because of their superior activity for low-temperature CO oxidation [32,33]. Geometric structures of a series of truncated octahedral nanoparticles with 38, 79, and 201 metal atoms were directly optimized with DFT and then were used for computing the CN^s of inequivalent surface Au sites. Figure 4 shows the parity plot between the model-predicted CO and O adsorption energies on core-shell alloy nanoparticles (Ag@Au and Cu@Au) and self-consistent DFT calculations. The agreement between the model and the full DFT calculations (root-mean-square error (RMSE) < 0.2 eV) indicates that the CN^α has the power to describe surface reactivity of both the pristine and alloy nanocatalysts within a consistent framework, and can be easily generalized to other materials.

To conclude, we propose the orbitalwise coordination number CN^α of an adsorption site as a reactivity descriptor for metal nanocatalysts. Compared with the semiempirical bond-counting methods, the new descriptor showed improved performance for describing the surface reactivity of metal nanoparticles with varying size, shape, and composition, attributed to its explicit consideration of lattice strains and metal ligands. Moreover, the CN^α has a solid physical foundation via a direct connection to the electronic structure of an adsorption site, and thus provides an intuitive link to the complex nature of chemical bonding at surfaces. This study opens up the possibility of developing adsorbate-specific descriptors and a new way for unraveling trends of the surface reactivity of metal nanocatalysts with defects, impurities, alloy additions, supports, etc.

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