Calculation of electron density of states for ensemble of gold nanoclusters

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Abstract. The method was developed for calculation of electronic properties of an ensemble of nanoclusters with the use of cluster perturbation theory. This method was applied to the ensemble with various geometry of gold nanoclusters with octahedral symmetry. The dependence of the density of electronic states on the mutual spatial arrangement of nanoclusters in the ensemble is obtained. It is shown that the metallic behavior of the ensemble maintains even when strong disorder is present.

1. Introduction
Metal nanoclusters possess unique physical and chemical properties, which differ from the properties of both bulk metals and individual atoms. In recent years, nanoclusters have attracted increased attention due to numerous possible applications in various fields from biomedicine [1] to nanoelectronics [2]. Existing widely accepted numerical methods of studying the electronic structure of many-body systems face serious difficulties when considering ensembles of metal nanoclusters, such as the need to take into account a large number of elements of the system when applying the density functional theory (DFT), or the sign problem in quantum Monte Carlo (QMC) algorithms. Cluster perturbation theory (CPT), introduced in [3] and developed in [4], uses the wave function of a single nanocluster to model the wave function of the ensemble, and accounts for the interaction between nanoclusters as single-particle hopping terms. CPT was successfully used to calculate the band structure of NiO [5], to obtain the ground-state phase diagram of $t - t' - t'' - U$ Hubbard model describing high-temperature cuprate superconductors [6], to estimate hopping integrals in fullerenes [7].

The purpose of the paper is to apply CPT for calculating electronic properties of a finite system, namely, an ensemble of gold nanoclusters. Analogously to [4], the entire system (an ensemble of nanoclusters) is considered to be composed of a finite number of structure elements, i.e. single nanoclusters. Each nanocluster is big enough so that the exact diagonalization method cannot solve the problem for one cluster because of the large size of the Hilbert space, therefore, the Green’s function for each nanocluster is calculated with the use of DFT technique. With the use of CPT, it became possible to model and investigate a realistic ensemble. The proposed technique is much less resource and time consuming compared to DFT and QMC.

2. Method
The ensemble of identical metal nanoclusters can be described by the following Hamiltonian,
\[ H = H_0 + V, \]  
(1)

where

\[ H_0 = \sum_R H^0_R, \quad V = \sum_{R, R'} V^{RR'} R^R_R R^R_R'. \]  
(2)

Here \( H^0_R \) is the Hamiltonian of a single nanocluster located at a radius-vector \( R \); \( V \) is the hopping term between nanoclusters; \( r \) is the combined index which counts the sites within a nanocluster and different orbitals on these sites.

The single nanocluster should be chosen so that it is possible to calculate its Green’s function within DFT approach; the obtained Green’s function has the form

\[ G^{DFT}_{\nu\nu'}(k, \omega) = \frac{\delta_{\nu\nu'}}{\omega + \mu - \varepsilon_{\nu}(k)}, \]  
(3)

where \( \varepsilon_{\nu}(k) \) is the band structure of the nanocluster; \( \nu \) defines the bands; \( \mu \) is the chemical potential.

To apply CPT, one should switch to the basis of localized orbitals,

\[ G^0_{\nu\nu'}(\omega) = \sum_k \sum_{\nu\nu'} P_{\nu\nu}(k, \omega) G^{DFT}_{\nu\nu'}(k, \omega) P^*_{\nu'\nu'}(k, \omega), \]  
(4)

where \( P_{\nu\nu}(k, \omega) \) is the transition matrix; \( G^0_{\nu\nu'}(\omega) \) is the Green’s function of the single nanocluster.

At the first order of strong-coupling perturbation theory, the one-electron Green’s function of the whole system can be written in matrix form as [4]

\[ G(\omega) = \frac{G^0(\omega)}{1 - VG^0(\omega)}. \]  
(5)

Here \( G(\omega) \equiv G^0_{rr'}(\omega) \); \( V \) is the hopping matrix between clusters, which can be expressed in quite simplified form with the use of only two parameters, the amplitude \( t_0 \) and characteristic length \( l_0 \), as

\[ V^{RR'}(\omega) = -t_0 \exp \left( -\frac{r_R - r_R'}{l_0} \right), \]  
(6)

\( r_r \equiv \{ R, r \} \). The density of states of the ensemble is

\[ A(\omega) = -\frac{1}{\pi} \text{Im}(G(\omega)). \]  
(7)

3. Results

To apply the formalism introduced in the previous section, consider an ensemble of identical gold nanoclusters. Each nanocluster is consisted of 13 gold atoms, has the diameter of 5.66 Å, and possess octahedral symmetry (Fig. 1 (a)). Ab initio electronic structure calculations were performed within the DFT using very accurate full-potential linearized augmented planewave (FP-LAPW) approach as implemented in Wien2k code [8]. The Perdew, Burke, Ernzerhof (PBE) gradient corrected local density approximation (GGA) for the exchange correlation potential [9, 10] was used with 64 k-points in the first Brillouin zone. Then, \( G^0_{rr'}(\omega) \) was obtained by dmftproj TRIQS package [11], which appends Wien2k code and builds the transition matrix elements from electronic bands obtained by DFT, to the localized orbitals. Since the properties of an electron system are determined by the density of states near
the Fermi level, for gold we can confine ourselves to taking into account only the s- and d-orbitals, which give the main contribution. When the Green’s function in localized orbitals basis is known, (7) allows us to obtain DOS of the single nanocluster, which is shown in Fig. 1 (b). Isolated bands and sharp peaks are clearly visible; these features are caused by finite and small size of the nanocluster, which lead to dimensional quantization.

Figure 1. (a) Single nanocluster consisting of 13 gold atoms; (b) corresponding DOS calculated by DFT with the use of Wien2k code. Contributions of d-orbital at energies below \(-1\) eV, and s-orbital at the Fermi level and upper, can be identified. This orbital structure of DOS is similar to the one of bulk gold, where deep levels are formed by d-orbital, and the band structure near the Fermi level is determined by s-orbital.

Figure 2. Ensemble of 64 nanoclusters located at equal (a) and random (b) distances from each other.

To model an ensemble, we first have constructed a regular cubic lattice consisting of 64 Au\textsubscript{13} nanoclusters (Fig. 2 (a)). The distance between the centers of the clusters was equal to 10 Å. The density of states of such regular ensemble should have the same features as the DOS of the single nanocluster, except for the connections between the bands of dimensional quantization will appear. This can be clearly seen in Fig. 3 (blue line), as the DOS of the ensemble resembles the DOS of a bulk metal. To go further to more realistic situation, we have added the lattice disorder: the displacement of each
nanocluster was produced by normal random generator with variance $\sigma$ in the range from 0 (regular lattice) to 2Å. The configuration of the ensemble for $\sigma = 2$Å is shown at Fig. 2 (b).

![DOS of s-d-hybridized orbital of the ensemble of gold nanoclusters calculated by DFT with the use of Wien2k code for different values of variance $\sigma$.](image)

**Figure 3.** DOS of s-d-hybridized orbital of the ensemble of gold nanoclusters calculated by DFT with the use of Wien2k code for different values of variance $\sigma$.

Figure 3 shows the dependence of DOS of the ensemble on the variance $\sigma$. It can be seen that the value of disorder affects only those regions of DOS that have no contribution from dimensional quantization of single nanocluster. At the same time, with the increase of $\sigma$, the peaks in the region of Fermi energy disappear, and the tendency is observed of convergence of the DOS of the disordered ensemble to the DOS of single cluster. However, the initial density of the ensemble is sufficient to maintain the metallic behavior even when strong disorder is present.

4. Conclusions
In this paper, we have presented the method of calculating the density of electronic states of the ensemble of nanoclusters, which is based on the cluster perturbation theory. The method is computationally efficient since it required DFT calculation of only one nanocluster, and can be applied to numerous systems which are characterized by low symmetry and large sizes. This method will encounter difficulties when treating systems with complex hybridization, however, even in this case it will be able to obtain qualitatively satisfactory results.

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