# Small Pd clusters: A comparison of phenomenological and *ab initio* approaches

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The lowest-energy structures of small Pd clusters ($2 \le N \le 13$) are computed by means of available phenomenological many-body potentials and by *ab initio* methods. The lowest-energy configuration is found by means of a genetic algorithm search. Satisfactory agreement between the results of the several methods implemented is achieved. Of special interest is the fact that all phenomenological potentials yield the same symmetry group for the lowest-energy cluster geometries, which moreover are identical with *ab initio* results. This constitutes an indication that the most common many-body empirical potentials can be trusted to yield reliable results.

Clusters have recently attracted much attention due to their interest to basic science and because of their many present and potential technological applications.[1] In part the interest derives from the insights that clusters and nanoparticles provide into the evolution of physical and chemical properties between the atomic and molecular limits, on the one hand, and the bulk limit on the opposite extreme. On the more applied side, Fe clusters promote the nitrogen plus hydrogen conversion into ammonia and platinum clusters catalyze the process to increase the octane grade of gasoline. Palladium, in particular, is used to create catalytic lattices[2] and, because of its almost full *d* band, has unusual magnetic properties.

However, an ongoing controversy exists as to the minimum-energy configurations of metallic clusters.[3,4] In fact, often different *ab initio* implementations yield different geometries which barely differ in energy.[4] Since these *ab initio* calculations become quite formidable as the number of atoms in the cluster grows, the use of empirical potentials, in combination with efficient search algorithms, becomes an effective tool in the quest for the most stable cluster geometry. However, the use of empirical potentials is conditioned by the accuracy with which they yield the most stable (minimum-energy) structures. On the other hand, they have the advantage of allowing one to undertake molecular-dynamics calculations involving large clusters and even their collisions.[5]

Within this context this paper has a variety of objectives: (i) to contrast results obtained with the different available phenomenological potentials, (ii) to implement a powerful and efficient minimization procedure to compute the global energy minimum, and (iii) to compare the results obtained by the different approaches and contrast them, whenever feasible, with results available in the literature and with our own first-principles data.

On the other hand, it is also important to keep in mind that metals are not properly described by pair potentials. The many-body embedded-atom method (EAM) was put forward as an alternative to the use of the pair potential and assumes that each atom in a solid can be viewed as an impurity embedded in a host, which comprises all the rest of the atoms, so that the total electron density is approximated by the superposition of electron densities of individual atoms.[6,7] Thus, the electron density in the vicinity of each atom can be written as the sum of the local density plus the electron densities due to all the surrounding atoms. By making the simplifying assumption that this background density is constant,[6,7] an embedding energy is defined as a function of the background electron density for each particular atomic species.

Phenomenological potentials have been used extensively since they were introduced in the mid-1980s. Possibly the first successful attempt is due to Foiles, Baskes, and Daw[6,7] (FBD), who put forward the formalism known as the EAM. This formalism was improved upon by Voter and Chen[8] (VC). Other formalisms, different from the EAM, were put forward by Gupta[9,10] (G), Sutton and Chen[11] (SC), and, more recently, Murrell and Mottram[12,13] (MM). All of them use many-body potentials, which were fitted to experimental results, like the cohesive energy, lattice parameters, and independent elastic constants for the bulk 0-K crystal structure. In addition, we also use the state-of-the-art minimization strategy to obtain global energy minima, by means of genetic algorithms (GA's).[14–16] The main reason for doing so is that other methods, like Monte Carlo and conjugate gradient, show a strong tendency to get stuck in local minima. This problem is overcome by GA's, to make sure that the absolute minimum basin is located. Within this basin and as is well established,[17] GA procedures are combined with local minimizers to zero in on the local minimum. With this purpose in mind we implemented several local minimizers: classical molecular dynamics (MD), SIMPLEX, and Monte Carlo. This way, after renewing the GA population, the local minimum closest to each individual is determined, with a considerable convergence acceleration. This scheme has proven to be quite reliable.[17,18] The increased computational speed thus achieved allows one to implement evaluation intensive minimization procedures, like the GA itself.

As mentioned above we determine the global energy minimum via the GA, a search technique based on the principles of natural evolution.[14–16] It uses operators that are analogs of the evolutionary processes of mating or crossover, mutation, and natural selection, to explore the multidimen-

sional parameter spaces. In particular, we have implemented a steady-state GA, in which we specify the fraction of the population that is replaced in each generation and the fraction that remains unchanged (elitism). We used real numbers (the spatial coordinates of each atom) in our genome and the roulette wheel selection method for the choice of parents. The genetic operators are inversion, one mutation, and four crossover operators: the arithmetic and geometric means and the *N*- and 2-point crossover operators, as described by Niesse and Mayne.[17] The objective function is, of course, the energy, and the fitness score is obtained by dynamic linear scaling of the raw objective scores in each generation.

For a fixed number *N* of atoms in the cluster and for each of the potentials described above, we performed computations for ten different populations (each of them with 30 individuals). The initial atomic positions were chosen at random under the constraint that the average pair separation be between 0.7 and 1.3 of the bulk distance, but smaller than the interaction range. The elitism percentage adopted was 30%, and 5000 generations were explored. A combination of SIM-PLEX, Monte Carlo, and molecular dynamics methods was implemented to obtain the local minimum configuration.

The *ab initio* Car-Parrinello MD (CPMD) calculations reported here where performed in the framework of the spin-polarized density functional theory[19,20] (DFT) by using the Car-Parrinello approach.[21] The exchange-correlation term is described by the generalized gradient approximation (GGA) in the Becke-Lee-Yang-Pann (BLYP) implementation.[22,23] An alternative is to use instead the B3LYP implementation, which consists in adding three correction terms to the Becke correlation functional but, since the latter was designed mainly to describe small covalently bonded molecules and contains empirical parameters,[24] it is less convenient to carry out the metallic cluster calculations we are reporting here. Norm-conserving pseudopotentials[25] with *s* and *p* as nonlocal and *d* as local orbitals were used. As input for the *ab initio* calculations we took the geometries obtained by means of phenomenological potentials (specifically the Gupta potential) and all degrees of freedom were allowed to relax when runing the CPMD code. In the case of the dimer we have compared our results with published ones[3,4,26] and they agree within 3%. Wave functions were expanded in plane waves with a 70-Ry cutoff. Convergence with a larger cutoff was successfully checked to less than 1 meV/atom. To obtain the magnetic configuration and to study the influence of magnetism on the structural properties of the minimum-energy clusters obtained via GA's and using phenomenological potentials, we also calculated *ab initio* the minimal geometries for clusters of two, three, four, five, and seven atoms with different multiplicities (singlet, triplet, and quintuplet). For all of them the triplet turned out to be the minimum-energy state. The *ab initio* SIESTA calculations were performed within the framework of DFT,[19,20] using a basis set of strictly localized numerical pseudoatomic orbitals, as implemented in the SIESTA code.[27–29] The exchange-correlation energy was calculated within the local spin density approximation (LSDA) as parametrized by Perdew and Zunger.[30] Norm-conserving pseudopotentials,[25] in their nonlocal form, were used to describe the electron-ion interaction, including nonlinear core corrections.[31] In the SIESTA calcula-
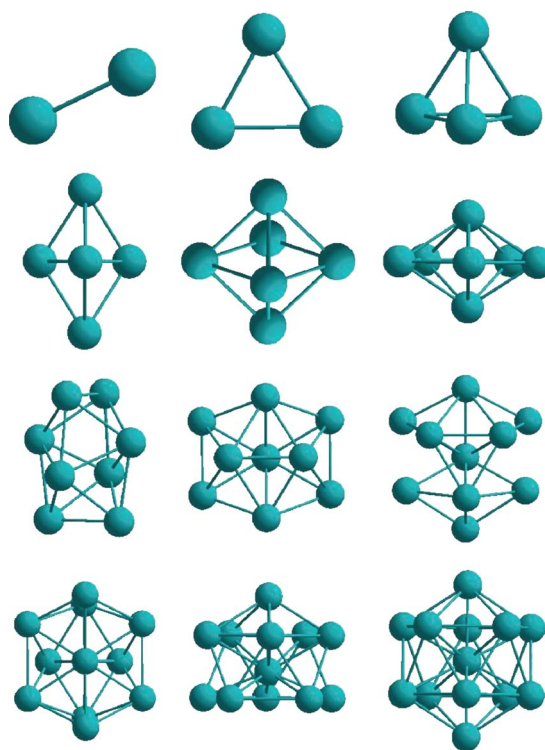


FIG. 1. (Color online) Optimized palladium geometries of clusters from 2 to 13 atoms in size.

tion we have used a double-zeta basis set including polarization functions (DZP).[28] Convergence tests have demonstrated that this basis yields reliable results in a variety of cases including covalent, ionic, and metallic systems. In fact, tests by Junquera *et al.* show that DZP calculations are comparable to well-converged plane-wave results.[32] The clusters were placed in a cubic supercell of up to 20 Å per side. Due to the large size of the supercell, only the $\Gamma$ point was used to sample the Brillouin zone. The cluster geometries obtained by means of the GA were fully relaxed using the conjugate gradient method, without any symmetry constraint, until all the force components became smaller than 0.05 eV/Å. The geometry of each cluster was minimized fixing the spin in different multiplicities from $S=0$ to 5. Our results show that for clusters with $N=2-7$ the minimum-energy spin configurations are triplet ($S=1$), for $N=8$ and 9 are quintet ($S=2$), for $N=10$ to 12 are septet ($S=3$), and for $N=13$ the minimum-energy state is a nonet ($S=4$). We also find that the Pd dimer yields a bond length of 2.45 Å and a binding energy of 1.21 eV/atom. The latter is in close agreement with the experimental value (1.03 eV/atom). For bulk Pd (fcc) we find a bond length of 2.725 Å,[33] which agrees well with the experimental value (2.748 Å).[34]

The geometries adopted by the minimum-energy Pd clusters, for $2 \leqslant N \leqslant 13$, are displayed in Fig. 1 where the symmetries that determine the point groups given in Table I are illustrated. These symmetries are consistent with recent reports,[35–37] but with minor differences. For $N=9$, for example, our results differ from Ref. 30, but agree with Refs. 31 and 32. Recently a nonichosaedral minimal structure was reported[4] for the $N=13$ cluster. However, at $T=0$ the energy

TABLE I. Interatomic distances (in Å) for various Pd clusters and their corresponding point-symmetry group (PG). The symbol † denotes average distances, whereas $^*$ indicates that these distances correspond to a triangular pyramid ($C_{3v}$), rather than to a regular tetrahedron ($T_d$). The two rows of $D_{3h}$ and $D_{5h}$ correspond to in and out of plane, while for $I_h$ they identify center to shell and intrashell distances.

| $N$ | PG | CPMD | SIESTA | FBD | VC | $G$ | SC | MM |
|---|---|---|---|---|---|---|---|---|
| 2 | $D_{\infty h}$ | 2.56 | 2.45 | 1.84 | 2.50 | 2.28 | 2.39 | 2.67 |
| 3 | $D_{3h}$ | 2.66† | 2.50 | 2.25 | 2.52 | 2.41 | 2.49 | 2.68 |
| 4 | $T_d$ | 2.68* | 2.58† | 2.39 | 2.55 | 2.49 | 2.55 | 2.69 |
| 5 | $D_{3h}$ | 2.75† | 2.69† | 2.53 | 2.59 | 2.56 | 2.60 | 2.70 |
|  |  | 2.68† | 2.59† | 2.41 | 2.55 | 2.51 | 2.56 | 2.69 |
| 6 | $O_h$ | — | 2.63† | 2.47 | 2.56 | 2.54 | 2.59 | 2.68 |
| 7 | $D_{5h}$ | 2.66† | 2.61† | 2.46 | 2.56 | 2.54 | 2.60 | 2.70 |
|  |  | 2.77† | 2.67† | 2.52 | 2.58 | 2.57 | 2.61 | 2.69 |
| 8 | $D_{2d}$ | — | 2.64† | 2.50† | 2.57† | 2.57† | 2.61† | 2.68† |
| 9 | $C_{2v}$ | — | 2.65† | 2.55† | 2.60† | 2.60† | 2.63† | 2.71† |
| 10 | $C_{3v}$ | — | 2.66† | 2.56† | 2.61† | 2.61† | 2.64† | 2.71† |
| 11 | $C_{2v}$ | — | 2.65† | 2.58† | 2.62† | 2.62† | 2.65† | 2.71† |
| 12 | $C_{5v}$ | — | 2.67† | 2.60† | 2.63† | 2.64† | 2.67† | 2.71† |
| 13 | $I_h$ | — | 2.61† | 2.52† | 2.55† | 2.55† | 2.58† | 2.62† |
|  |  |  | 2.75† | 2.65† | 2.68† | 2.69† | 2.71† | 2.76† |

difference between the two structures, ichosaedral and buckled biplanar, is tiny (0.02 eV). In addition, we also checked with SIESTA the strictly biplanar and cubeoctahedral configurations. The strictly biplanar has lower energy, but differs from the buckled biplanar by only 0.19 eV. All of them have larger energies than the icosahedral structure. Moreover, we are at present implementing a different global minimization procedure (conformational space annealing),[38] which also yields, in combination with phenomenological potentials, several of the preceding structures separated by small energy differences.

In Fig. 2 the average nearest-neighbor distance is plotted as a function of cluster size for the different potentials used. Each value corresponds to the arithmetic average of ten runs, carried out for every value of $N$ (the number of atoms in the cluster) and for every potential. Starting from the dimer, the bond lengths increase with increasing cluster size to a value
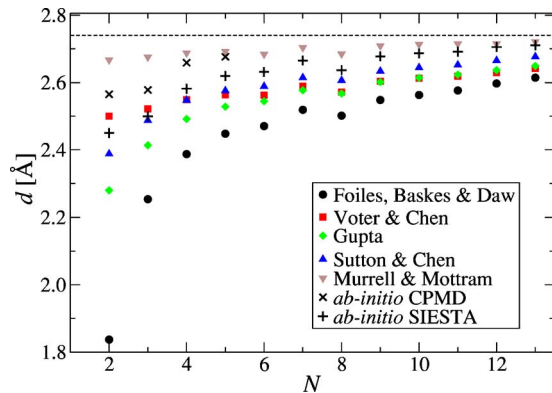


FIG. 2. (Color online) Average nearest-neighbor distance for the various empirical potentials and *ab initio* methods we implemented. The dashed line is the experimental bulk value.

larger than 2.6 Å. For the dimer, the accepted value[33,39] is 2.48 Å. Examination of Fig. 2 indicates that overall, for our phenomenological calculations, the Sutton-Chen potential yields the best results; the largest deviations, compared to *ab initio* results, are given by the Foiles-Baskes-Daw potential. Previous results for bond lengths differ only slightly with ours. Our VC potential bond length for the dimer is shorter, and for the rest of the clusters longer, than that of Karabacak *et al.*,[35] also obtained with the VC potential. Our SIESTA results are slightly shorter than those of Kumar and Kawazoe[37] and Nava *et al.*,[36] obtained using other DFT implementations.

In order to investigate the relative stability of the clusters we consider the evolution of the binding energy $E_b$ and the first and second energy differences $\Delta^{(1)}E$ and $\Delta^{(2)}E$, respectively, all defined in terms of the total interaction energy of the cluster $V_{\text{cluster}}$. Analytically

$$E_b(N) = \frac{V_{\text{cluster}}}{N}, \tag{1}$$

$$\Delta^{(1)}E = E_b(N) - E_b(N-1), \tag{2}$$

$$\Delta^{(2)}E = 2E_b(N) - E_b(N-1) - E_b(N+1). \tag{3}$$

Our results for $E_b$ as a function of $N$ are displayed in Fig. 3. In the *ab initio* calculations $E_b$ was obtained by subtracting $N$ times the energy of an isolated Pd atom. In the $N \gg 1$ limit $E_b$ will approach the bulk cohesive energy (for Pd it is $E_b^{bulk} = -3.89$ eV/atom). In terms of stability, the extent to which $E_b$ and $\Delta^{(1)}E$ differ is a signature of how far apart the clusters are from the bulk limit. An important feature of the $E_b(N)$ graph, displayed in Fig. 3, is the dip in the vicinity of $N=13$, which corresponds to a region of enhanced stability (magic number). For clusters of sizes in the range $4 \leqslant N$
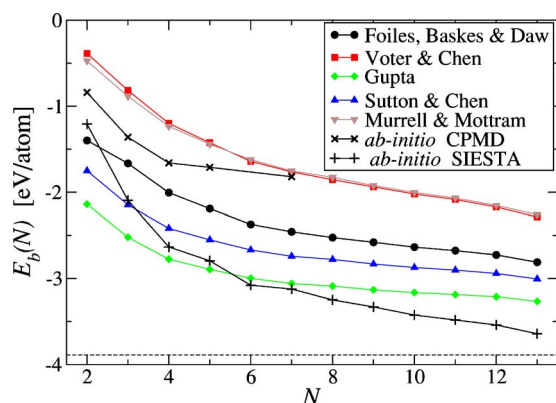
FIG. 3. (Color online) Energy per atom, as a function of cluster size. The dashed line corresponds to the bulk limit.



FIG. 4. (Color online) Second energy difference results.

$\leq 13$ we calculated again, using as input for SIESTA, the cluster configurations obtained with the Gupta potential and illustrated in Fig. 1. We also calculated, using SIESTA, the energies of the $N=4$, 5, and 6 planar configurations[3] and found that these structures are 0.9, 1.6, and 3.1 eV higher in energy than the nonplanar ones, confirming that the clusters in Fig. 1 have lower energies.[3]

Moreover, a minimum of $\Delta^{(2)}E$ indicates an enhanced stability of a cluster of $N$ atoms, relative to its heavier and lighter neighbors. Therefore, $\Delta^{(2)}E$ can be considered a measure of the stability of the clusters, which in general is correlated with experimental mass spectral intensities, rather than with the binding energy $E_b$. Large negative minima of $\Delta^{(2)}E$ identify the clusters which are most stable. Figure 4 displays our results for the second finite difference of the total energy plotted against cluster size. Except for the Murrel-Mottram potential results for $\Delta^{(2)}E$ the agreement of the data is quite satisfactory.

In conclusion, we calculated by means of the available empirical many-body potentials, and also by two *ab initio* implementations, the physical properties of small palladium clusters ($2 \leq N \leq 13$). These computations were combined with a state-of-the-art search algorithm (GA) to obtain global energy minima. All the methods employed yield results that are quite similar as far as the general trends are concerned. It is especially remarkable that all the phenomenological potentials yield the same symmetry group for the lowest-energy cluster geometries. In addition, within our scheme, the *ab initio* codes also yield the same symmetry. Differences of less than 10% in the interatomic distances, for clusters with more than five atoms, appear as a consequence of using a particular computation scheme. While, as expected, phenomenological potentials do not yield good results for very small
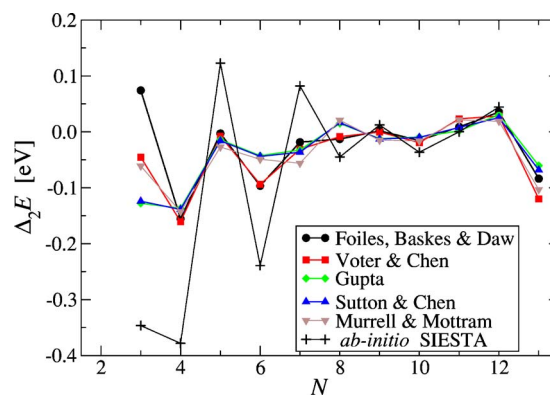
clusters, which on the other hand can be handled *ab initio* without any trouble, the agreement improves rapidly as $N$ grows. In fact, a computer time saving strategy is to use the geometry obtained with any of the above-mentioned phenomenological potentials and rescale the distances via an *ab initio* procedure. This way, the use of phenomenological potentials allows us to reliably determine the symmetry of the minimum-energy configurations and to save time in the determination of the interatomic distances.

In principle one does expect *ab initio* procedures to be the definitive tool to handle cluster physics problems; however, it is not always feasible (or at least practical) to implement such calculations, be it because the number of atoms involved is too large or because one wants to tackle problems which require one to compute a large number of different configurations, like the full treatment of cluster-cluster collisions.[5] While progress has been made in the description of excitation and relaxation processes in atom-cluster collisions—for example, by Saalman and Schmidt[40] who combined time-dependent DFT and classical molecular dynamics—even these calculations are quite formidable. Thus, the fact that empirical many-body potentials can be trusted to yield a reasonable description of the physics of clusters, in particular when *ab initio* calculations are not feasible, as for example in the study of cluster-cluster collisions, is quite gratifying.

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