

An accurate description of quantum size effects in InP nanocrystallites over a wide range of sizes

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Abstract

We obtain an effective parametrization of the bulk electronic structure of InP within the Tight Binding scheme. Using these parameters, we calculate the electronic structure of InP clusters with the size ranging upto 7.5 nm. The calculated variations in the electronic structure as a function of the cluster size is found to be in excellent agreement with experimental results over the entire range of sizes, establishing the effectiveness and transferability of the obtained parameter strengths.

PACS No. 61.46.+w, 73.22.-f

Effect of quantum confinement on electronic properties of semiconductors has been a subject of intense study in the recent years [1] due to their potential applications in various devices [2]. In the nanometer regime, where the extensions of the electron and hole wave functions are constrained by the particle size, the electronic and optical properties are drastically different from the bulk material. For example, the band gap of a semiconductor such as CdS can be varied from its bulk value of 2.5 eV to about 4.5 eV for ~ 2 nm sized clusters [3]. This size quantization effect can be qualitatively explained by the simplest quantum mechanical particle-in-a-box problem where, upon decreasing the size of the box, the energy separation between various levels increases due to the confinement. Quantitatively, the effective mass approximation (EMA) [4] describes such a size dependent energy shift. The EMA, though suitable for larger clusters, fails to correctly predict the band gap variation with the size for smaller clusters, grossly overestimating the band gap of the small sized semiconductor nanoparticles. Starting from the atomic limit, the *ab initio* approaches, though accurate and hence desirable, prove to be computationally expensive even for small sized (~ 1.5 nm) clusters [5]. An intermediate approach that uses screened atomic pseudopotentials obtained from self-consistent first principle calculations has been applied to II-VI semiconductors [6] and recently to InP [7, 8]. The results are encouraging but this technique too becomes computationally demanding for larger clusters; moreover, such approaches are also somewhat empirical in nature in contrast to the first principle calculations. Since quantum confinement effects are appreciable for cluster sizes comparable to the excitonic diameter in the bulk, which can be as large as 15 nm in InP, it is obvious that an alternate methodology is required to treat this problem. A semi-empirical tight-binding (TB) scheme that borrows parameters from the bulk band structure is less time consuming and has been applied with reasonable success to II-VI [9], III-V [10] and group IV [10, 11] semiconductors though the transferability of bulk parameters to the nanometer regime is a controversial issue. Our recent attempts [12, 13] in this direction suggest that some of the difficulties arise from an improper or inaccurate tight binding (TB) parametrization of the bulk band structures. It has been observed that the nearest neighbor only model cannot describe the band structure accurately and that inclusion of the next nearest neighbor interactions in the basis set is necessary to obtain a good description of the bulk band dispersions. [13] In the present letter, we show for InP that a proper parametrization that includes the next nearest neighbor interactions leads to an excellent description of experimental results

over the entire range of sizes.

Following our recent successful approach, [13] we employ a TB method with the sp^3 orbital basis on In atom and the sp^3d^5 orbital basis on the P atom. Along with the nearest neighbor In-P interactions, our model also includes the second nearest neighbor, In-In and P-P interactions. The s^* orbital used in the earlier TB models [9, 10, 14] is not required in the present approach.

The TB Hamiltonian is given by

$$\mathbf{H} = \sum_{il} \epsilon_{il} a_{il}^\dagger a_{il} + \sum_{ij} \sum_{l'l''} (t_{ij}^{l'l''} a_{il}^\dagger a_{jl''} + \text{h.c.}) \quad (1)$$

where a_{il}^\dagger and a_{il} are respectively the creation and annihilation operators for electrons at the atomic site, i in the l^{th} orbital. The onsite energy for the orbital l at the site i is given by ϵ_{il} . The hopping interaction strengths $t_{ij}^{l'l''}$ depend on the type of orbital and geometry of the lattice and are parametrized using the Slater-Koster scheme [15]. In order to obtain the best estimates for the onsite energies and the Slater-Koster parameters, we obtained the band dispersions in InP along various symmetry directions using the Linearized Muffin Tin Orbitals within the Atomic Sphere Approximation (LMTO–ASA), after converging the calculations with 43 k points in the irreducible part of the Brillouin Zone. [16] The band gap obtained from the LMTO method is 0.63 eV; an underestimation of the experimental value of 1.4 eV. Thus, we correct the band gap to match the experimental value by shifting the unoccupied bands by the appropriate amount. Then, we fit these *ab-initio* band dispersions with those obtained from the TB model within a least-squared-error approach by varying the TB parameter values. Fig. 1 shows the comparison between LMTO band dispersions and the TB fitted band dispersions with optimized parameter values (Table I), exhibiting an excellent agreement over the entire valence and conduction bands. It should be noted here that it is not sufficient to get only the energies at various symmetry points accurately described, as has been emphasized in the past. The effective electron mass from our LMTO and TB calculations, deduced from the curvature of the lowest conduction band, are 0.084 and 0.09, respectively, showing an excellent fit of the curvature of the band dispersions near the Γ point. They are also in good agreement with the reported experimental values ranging between 0.068 to 0.084. [17] In order to describe the evolution of the electronic structure of clusters with the size, it is absolutely essential to obtain a reliable description of the curvature of the band dispersion at

the extremal points. The reliability of the present model and the parameters obtained arises from an accurate description of both the energies and the curvatures. [18]

Similar to our previous studies of Mn-doped GaAs nanoparticles, [19] the clusters we generate consist of a central In atom surrounded by the four nearest neighbor P atoms, followed progressively by shells of In and P atoms, respectively. The effective diameter of the cluster is calculated assuming that the particles are spherical in shape using the formula

$$d = a \left[\frac{3N_{at}}{4\pi} \right]^{1/3} \quad (2)$$

where a is the bulk lattice parameter (5.861 Å for InP [20]) and N_{at} is the number of atoms in the cluster. In our calculations, the largest cluster has $N_{at} = 9527$ atoms and a diameter of 77.1 Å containing 60328 orbitals. We passivate the clusters with hydrogen atoms at the outermost layer to remove the dangling bonds and obtain the eigen-value spectrum for clusters with different sizes using the Lanczos algorithm [21].

Variations of energies of the top of the valence band (TVB) and the bottom of the conduction band (BCB) as a function of cluster diameter are shown in Fig. 2. The results clearly show the systematic shifts of both TVB and BCB away from those of the bulk, marked by dashed lines, with decreasing cluster size as a consequence of quantum confinement. The positions of TVB and BCB for four specific cluster sizes have been reported in Ref. [8]; we show these results in the same figure indicating a good agreement for the common range of sizes. [29] In order to compare the present results with the experimental estimates of band edges obtained from the optical absorption experiments, it is necessary to take into account the excitonic binding energies at different cluster sizes; we use the form [22] $3.572 * e / \epsilon d$ for the excitonic binding energy, where d is the diameter of the cluster and ϵ is the dielectric constant, 12.4 for InP. Thus derived calculated band-gap variation with cluster size is shown in the inset in Fig. 3, exhibiting a systematic and pronounced variation. The dependence of the band gap on the diameter of the cluster is expected to be given by an inverse square, $1/d^2$, law according to EMA. However, such a relationship is completely incompatible with the present results. We find that $1/d^x$ with $x = 1.04$ provides the best fit of the calculated results, as shown by the dotted line in the inset, suggesting an approximately $1/d$ dependence, instead of the $1/d^2$ one. However, this fit is not satisfactory, particularly for large cluster sizes (see inset, Fig. 3). We find

that the expression, $100*(5.8d^2+27.2d+10.4)^{-1}$, provides a good description of the band gap variation with the cluster diameter over the entire range of sizes, as shown by the solid line in the inset.

The variation of the band gap, ΔE_g , with respect to the bulk band gap is compared with experimental values and with results obtained from other calculations in the main frame of Fig. 3. The excellent agreement of the present calculated results with the experimental data [23, 24, 25, 26] over the entire range of sizes is evident from this comparison. The expected band gap variation on the basis of EMA [27], shown in the figure with a thin line, is in gross disagreement with the experimental results. Though the parameterized pseudopotential result [8] qualitatively predicts the variation of band gap accurately and tends to agree with the experimental band gap as one approaches the atomic limit and the bulk limit, it slightly underestimates the band gap in the nanometer regime. The $sp^3d^5s^*$ parametrization scheme that was recently reported [10] overestimates the band gap systematically over the entire range of sizes [28].

In conclusion, we have shown that an effective parametrization within the tight binding model allows us to describe the bulk electronic structure of InP without the need to invoke the fictitious s^* orbital. We have also established the transferability of these parameters to obtain electronic structures of clusters over a wide range of sizes; thus calculated variation in the band gap with the cluster size is in excellent agreement with experimental results. Taking into account the accuracy of this method, the ease of implementation and the computational cost, it should be possible to apply this method to perform molecular dynamics of large clusters.

We thank O. K. Aderssen and O. Jepsen for the LMTO codes, P. Mahadevan for the LAPW calculations and the Department of Science and Technology for funding the project.

References

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- [28] The Coulomb interaction term has been subtracted from the calculations of Ref. [10] which uses the $sp^3d^5s^*$ orbital basis in the TB model.
- [29] The results of Ref. [8] were rigidly shifted in order to ensure that the zero of the energy scale coincided with the top of the valence band in order to be consistent with the present convention.

Figure 1: Band structure obtained from LMTO and fitted using TB parametrization for bulk InP. The zero of the energy corresponds to the top of the valence band.

Figure 2: Variation of top of the valence band (TVB) and bottom of the conduction band (BCB) with effective diameter of the clusters. The pseudopotential results from Ref. [8] are also shown. The dashed lines show the TVB and the BCB for bulk InP.

Figure 3: Comparison of calculated band gap variation with experimental data and other theoretical results. The inset shows the $100 * (5.8d^2 + 27.2d + 10.4)^{-1}$ fit (solid line) and the $1/d^{1.04}$ fit (dotted line) to the present calculations.

Table I

TB parameters (in eV) obtained from least squared error fit to LMTO band dispersions for InP and parameters for hydrogen passivation.

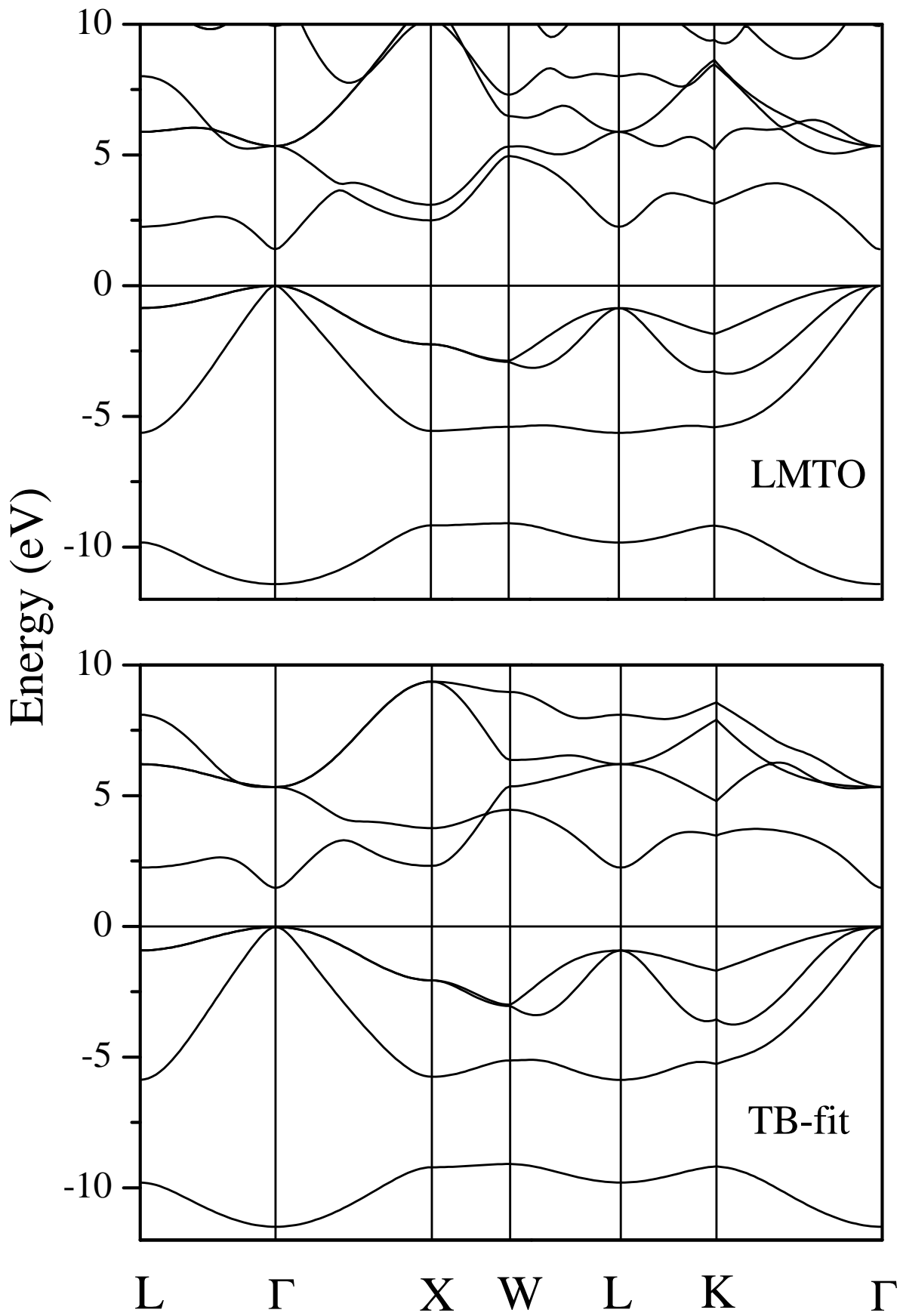
Onsite Energies

	s	p	d
In	-1.53	3.92	
P	-10.24	-0.63	16.62
H	-0.7412		

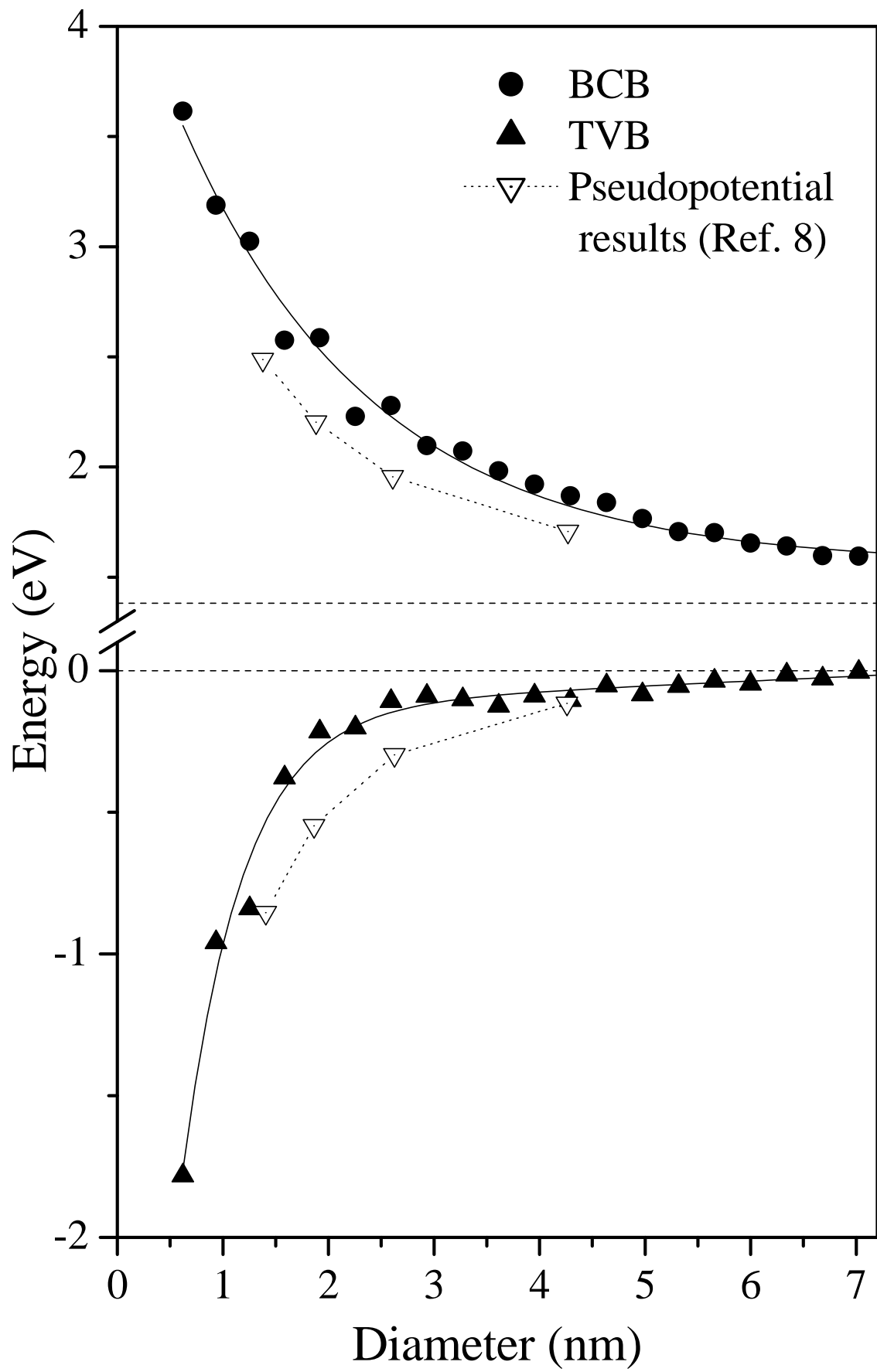
Slater Koster Parameters

	$ss\sigma$	$sp\sigma$	$sd\sigma$	$ps\sigma$	$pp\sigma$	$pp\pi$	$pd\sigma$	$pd\pi$
In-P	-1.43	2.19	-2.72	-1.63	3.35	-0.66	-3.38	3.35
In-H	-2.944	2.76	-1.36					

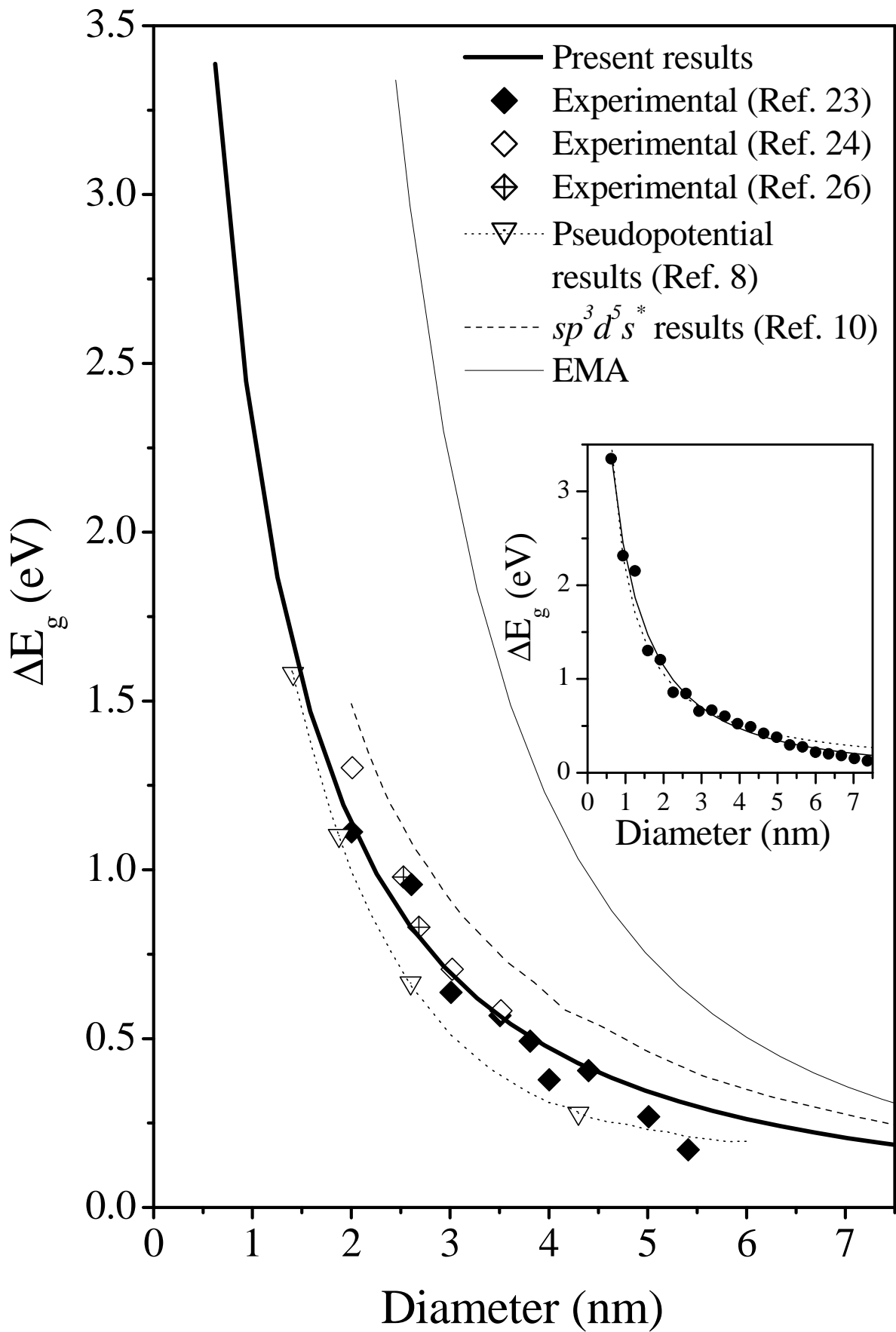
	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$
In-In	-0.21	0.00	0.14	-0.01
P-P	-0.01	0.14	0.70	-0.02



Sapra et al., Fig. 1



Sapra et al., Fig. 2



Sapra et al., Fig. 3