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# Basis set and electron correlation effects in all-electron *ab initio* calculations of the static dipole polarizability of small cadmium selenide clusters, (CdSe)<sub>n</sub>, *n* = 1,2,3,4

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## Abstract

We have calculated static dipole polarizabilities for small cadmium selenide clusters relying on finite-field Møller–Plesset perturbation theory and coupled cluster calculations. In addition to the conventional *ab initio* methods we have also used easily accessible density functional theory (DFT) based approximations. To avoid systematic errors, we have employed two sequences of purpose-oriented basis sets built upon drastically different substrates. Our findings reveal significant patterns in the performance of conventional *ab initio* and DFT methods. Of particular importance is the systematic divergence of the performance of the B3LYP and B3PW91 DFT methods:  $\bar{\alpha}(\text{B3LYP}) > \bar{\alpha}(\text{B3PW91})$  and  $|\Delta\alpha(\text{B3LYP})| > |\Delta\alpha(\text{B3PW91})|$  for (CdSe)<sub>n</sub>,  $2 \leq n \leq 4$ .

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**Keywords:** CdSe; Clusters; Polarizability; Ab initio; DFT

## 1. Introduction and theory

Cadmium sulfide (CdS) and cadmium selenide (CdSe) clusters are currently attracting much attention due to the emergence of particularly promising applications in materials science. Recent experimental work includes nonlinear susceptibility measurements on CdS clusters [1], nanoparticles [2] and thin films of CdS nanocrystals [3]. Work on CdSe includes measurements of electrostatic properties of CdSe nanocrystals by EFM (electrostatic force microscopy) [4], the determination of fluorescence quantum yield of CdSe/ZnS nanocrystals [5] and the observation of white light emission from magic-sized CdSe nanocrystals [6]. On

the other hand, systematic theoretical work on CdS and CdSe clusters is limited. Troparevsky and Chelikowsky used a pseudopotential approach based on the local density approximation (LDA) to determine molecular structures and polarizabilities for small CdS and CdSe clusters [7]. A theoretical study of the molecular geometry of CdS and CdSe clusters up to the heptamer was reported by Deglmann et al. [8]. Maroulis and Pouchan reported *ab initio* and DFT calculations of the polarizability and hyperpolarizability of small CdS clusters [9]. More recently, Karamanis et al. [10] obtained *ab initio* and DFT molecular geometries and polarizabilities for (CdSe)<sub>n</sub>, *n* = 1,2,3,4. The polarizability of the bulk CdSe is known from the excellent study of Rabani et al. [11].

Two major problems dominate the extension of theoretical investigations of electric (hyper)polarizability to medium and large sized CdSe clusters. First, the application of *ab initio* methods of high predictive capability is limited to small clusters. The DFT based methods are considerably more economic. Second, one can hardly rely on

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standard basis sets for calculations on  $(\text{CdSe})_n$  systems. Consequently, the construction of reasonably sized, flexible basis sets is a priority. In previous work, we examined closely the relative merit of DFT methods on several classes of molecular systems [12–16]. What is more, we have carefully demonstrated that basis set quality is of major importance in electric polarizability calculations: the construction of purpose-oriented basis sets is a key element of such studies [17–21]. In this paper we have constructed two different classes of basis sets. Our goal is to test the capability of small-sized but suitably optimized basis sets to predict reliable polarizability values for small CdSe clusters.

The energy of a neutral molecular interacting with a weak static electric field can be expanded as [22,23]

$$\begin{aligned} E^p &\equiv E^p(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, F_{\alpha\beta\gamma\delta}, \dots) \\ &= E^0 - \mu_\alpha F_\alpha - (1/3)\Theta_{\alpha\beta}F_{\alpha\beta} - (1/15)\Omega_{\alpha\beta\gamma}F_{\alpha\beta\gamma} \\ &\quad - (1/105)\Phi_{\alpha\beta\gamma\delta}F_{\alpha\beta\gamma\delta} + \dots - (1/2)\alpha_{\alpha\beta}F_\alpha F_\beta \\ &\quad - (1/3)\mathbf{A}_{\alpha,\beta\gamma}F_\alpha F_{\beta\gamma} - (1/6)\mathbf{C}_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta} \\ &\quad - (1/15)\mathbf{E}_{\alpha,\beta\gamma\delta}F_\alpha F_{\beta\gamma\delta} + \dots - (1/6)\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma \\ &\quad - (1/6)\mathbf{B}_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta} + \dots \\ &\quad - (1/24)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + \dots \end{aligned} \quad (1)$$

where  $F_\alpha$ ,  $F_{\alpha\beta}$ , etc. are the field, field gradient, etc. at the origin.  $E^0$ ,  $\mu_\alpha$ ,  $\Theta_{\alpha\beta}$ ,  $\Omega_{\alpha\beta\gamma}$  and  $\Phi_{\alpha\beta\gamma\delta}$  are the energy and the dipole, quadrupole, octopole and hexadecapole moment of the free molecule. The second, third and fourth-order properties (in bold) are the dipole and quadrupole polarizabilities and hyperpolarizabilities  $\alpha_{\alpha\beta}$ ,  $\beta_{\alpha\beta\gamma}$ ,  $\gamma_{\alpha\beta\gamma\delta}$ ,  $\mathbf{A}_{\alpha,\beta\gamma}$ ,  $\mathbf{C}_{\alpha\beta,\gamma\delta}$ ,  $\mathbf{E}_{\alpha,\beta\gamma\delta}$  and  $\mathbf{B}_{\alpha\beta,\gamma\delta}$ . The subscripts denote Cartesian components. A repeated subscript implies summation over  $x$ ,  $y$  and  $z$ . The number of independent components needed to specify the respective tensors is regulated by symmetry [22]. We have shown in previous work that relying on the finite-field method [24] it is possible to extract all electric moments and polarizabilities from the expansion of Eq. (1) [17,20,25].

In addition to the Cartesian components we also compute the mean ( $\bar{\alpha}$ ) and the anisotropy ( $\Delta\alpha$ ) of the polarizability. In the molecular orientation adopted in this work (see Fig. 1) the two invariants are defined as follows: for the monomer, with  $z$  as the molecular axis,

$$\begin{aligned} \bar{\alpha} &= (\alpha_{zz} + 2\alpha_{yy})/3 \\ \Delta\alpha &= \alpha_{zz} - \alpha_{yy} \end{aligned} \quad (2)$$

For the dimer,  $yz$  is the molecular plane and

$$\begin{aligned} \bar{\alpha} &= (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \\ \Delta\alpha &= 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2} \end{aligned} \quad (3)$$

For the trimer, with  $y$  as the  $C_3$  axis,

$$\begin{aligned} \bar{\alpha} &= (\alpha_{yy} + 2\alpha_{zz})/3 \\ \Delta\alpha &= \alpha_{yy} - \alpha_{zz} \end{aligned} \quad (4)$$

For the tetramer, there is only one independent component for  $\alpha_{\alpha\beta}$ , so  $\bar{\alpha} \equiv \alpha$  and  $\Delta\alpha = 0$ .

All methods used in this work are presented in sufficient detail in standard textbooks [26–28]. Møller–Plesset perturbation theory (MP) is a performant tool at relatively low computational cost. Coupled cluster (CC) techniques are characterized by high predictive capability but at a prohibitive computational cost even for medium sized molecules. The DFT based B3LYP and B3PW91 methods are now applied to wide classes of problems. In brief,

SCF	self-consistent field
MP2	second-order MP
SDQ-MP4	partial fourth-order MP with single, double and quadruple excitations from the reference determinant.
MP4	fourth-order MP
CCSD	singles and doubles CC
CCSD(T)	CCSD with an estimate of connected triple excitations by a perturbational treatment
B3LYP	B3:Becke's three-parameter hybrid functional
LYP	The correlation functional of Lee, Yang, and Parr which includes both local and non-local terms.
B3PW91	PW91:Perdew and Wang's 1991 gradient-corrected correlation functional.
B3:	as in B3LYP.

## 2. Computational strategy

The computational philosophy underlying the construction of basis sets has been expanded in previous work [17,20]. We design purpose-oriented basis sets by augmenting judiciously chosen substrates with diffuse Gaussian-type functions (GTF) and polarizability optimal polarization GTF. The optimal d-GTF exponents are chosen to maximize the mean polarizability  $\bar{\alpha}$ .

We use two sequences of basis sets in this paper. The first is built upon the 3-21G split valence substrate [29]

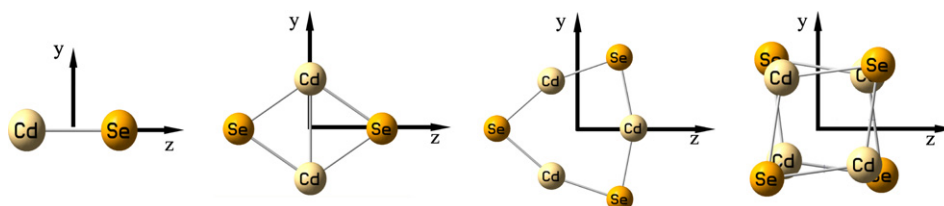
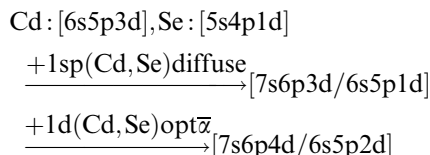


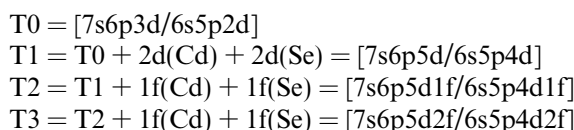
Fig. 1. Molecular orientations adopted in this work.

and consists of SV0, SV1 and SV2. Schematically, SV0 is designed as



The larger basis sets are SV1  $\equiv [7s6p5d/6s5p4d] = \text{SV0} + d(\text{Cd}) + d(\text{Se})$  and SV2  $= \text{SV1} + 1f(\text{Cd}) + 1f(\text{Se})$ . The impact of the optimal d-GTF is clearly seen in Figs. 2 and 3: the optimal exponents  $\eta_d(\text{Cd})$  and  $\eta_d(\text{Se})$  are defined quite sharply.

The second sequence T0, T1, T2 and T3 is built upon a Cd:[6s4p2d] [30], Se:[5s4p1d] [31] substrate. Schematically,



5D and 7F GTF were used on all basis sets.

All calculations in this work pertain to the molecular geometries previously reported [10] (see Fig. 1). The shapes of the HOMO–LUMO and the respective gaps (at the B3LYP/SV0 level of theory) are shown in Fig. 4. A more comprehensive presentation of these will be presented in future work, with the inclusion of results on larger cadmium selenide clusters.

In subsequent post-Hartree–Fock treatments for the monomer (CdSe) the 27 innermost MO were kept frozen. For the dimer, trimer and tetramer the number of frozen MO was 54, 81 and 108, respectively.

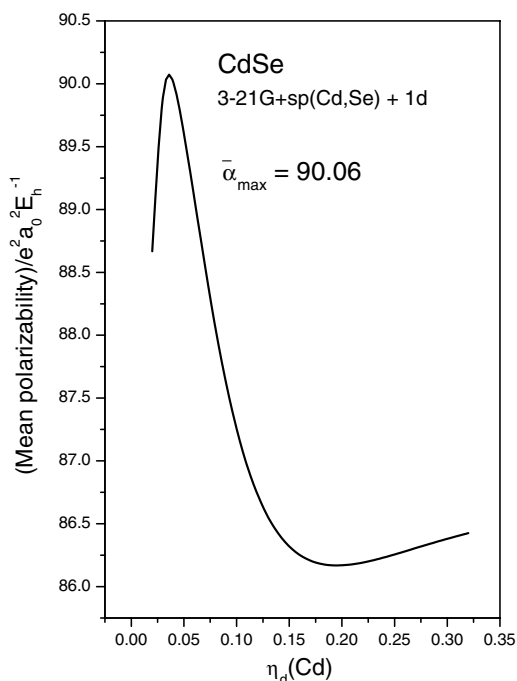


Fig. 2. Variation of the mean polarizability with the exponent of the diffuse d-GTF added on Cd.

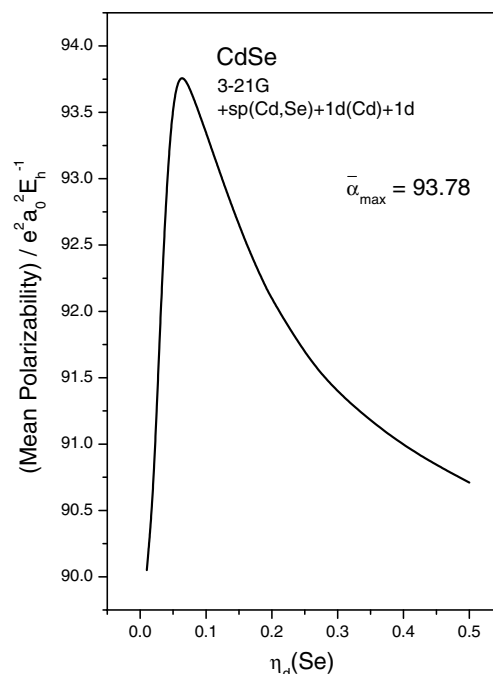


Fig. 3. Variation of the mean polarizability with the exponent of the diffuse d-GTF added on Se.

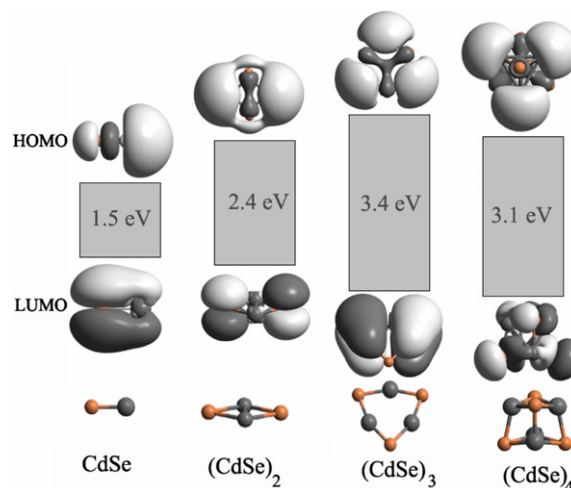


Fig. 4. HOMO and LUMO and the respective gaps in  $(\text{CdSe})_n$ ,  $n = 1-4$ .

All calculations were performed with the GAUSSIAN 98 set of programmes [32].

Atomic units are used throughout this paper. SI conversion factors are Energy,  $1 E_h = 4.3597482 \times 10^{-18} \text{ J}$ , Length,  $1 a_0 = 0.529177249 \times 10^{-10} \text{ m}$ , dipole moment  $\mu$ ,  $1 e a_0 = 8.478358 \times 10^{-30} \text{ Cm}$  and dipole polarizability,  $\alpha$ ,  $1 e^2 a_0^2 E_h^{-1} = 1.648778 \times 10^{-41} \text{ C}^2 \text{m}^2 \text{J}^{-1}$ . Hereafter, property values are given as pure numbers, that is,  $\mu/e a_0$  and  $\alpha/e^2 a_0^2 E_h^{-1}$ .

### 3. Results and discussion

Conventional *ab initio* results for all molecules are shown in Tables 1–4. B3LYP and B3PW91 values are given in Tables 5–8.

Table 1  
*Ab initio* dipole moment and polarizability for CdSe

Method	$\mu_z$	$\alpha_{xx} = \alpha_{yy}$	$\alpha_{zz}$	$\bar{\alpha}$	$\Delta\alpha$
<i>SV0</i>					
SCF	−3.2752	74.75	131.86	93.79	57.11
MP2	−2.9138	78.71	116.03	91.15	37.32
SDQ-MP4	−2.7148	80.94	129.12	97.00	48.17
MP4	−2.6400	81.59	123.63	95.60	42.04
CCSD	−2.7144	82.91	131.72	99.18	48.81
CCSD(T)	−2.6202	85.93	129.80	100.55	43.87
<i>SV1</i>					
SCF	−3.2286	74.23	132.61	93.69	58.38
MP2	−2.8432	78.02	116.17	90.74	38.15
SDQ-MP4	−2.6618	80.17	128.61	96.32	48.44
MP4	−2.5778	80.90	123.30	95.03	42.40
CCSD	−2.6627	81.93	131.77	98.54	49.85
CCSD(T)	−2.5597	84.86	130.32	100.02	45.45
<i>SV2</i>					
SCF	−3.2269	74.56	132.33	93.82	57.77
MP2	−2.8337	78.95	115.92	91.27	36.98
SDQ-MP4	−2.6567	80.81	128.14	96.59	47.33
MP4	−2.5725	81.74	122.76	95.41	41.03
CCSD	−2.6592	82.45	131.38	98.76	48.93
CCSD(T)	−2.5569	85.44	129.91	100.26	44.47
<i>T0</i>					
SCF	−3.2944	76.55	131.17	94.76	54.61
MP2	−2.6988	85.23	119.47	96.64	34.25
SDQ-MP4	−2.5294	86.60	126.32	99.84	39.73
MP4	−2.4849	86.00	119.76	97.25	33.76
CCSD	−2.5186	90.99	134.53	105.51	43.54
CCSD(T)	−2.4813	92.83	131.76	105.81	38.93
<i>T1</i>					
SCF	−3.2894	74.80	130.64	93.42	55.83
MP2	−2.7658	79.85	117.13	92.28	37.27
MP3	−2.6616	81.83	129.55	97.74	47.72
MP4	−2.4738	82.09	121.77	95.32	39.67
CCSD	−2.5912	84.35	131.44	100.05	47.09
CCSD(T)	−2.4740	88.36	129.26	101.99	40.90
<i>T2</i>					
SCF	−3.2918	75.00	130.86	93.62	55.86
MP2	−2.7662	80.40	117.04	92.62	36.64
SDQ-MP4	−2.5827	82.06	127.86	97.33	45.79
MP4	−2.4751	82.62	121.58	95.61	38.96
CCSD	−2.5939	84.58	131.47	100.21	46.89
CCSD(T)	−2.4760	88.57	129.32	102.15	40.74
<i>T3</i>					
SCF	−3.2915	75.04	130.91	93.66	55.87
MP2	−2.7656	80.43	117.09	92.65	36.65

**CdSe.** The dipole moment of the monomer is stable enough at the SCF level of theory. Our best values for this property are  $\mu = -3.2269$  (SV2) and  $-3.2915$  (T3). Electron correlation lowers significantly the magnitude of this property. The CCSD(T) values obtained with SV2 and T2 are  $-2.5569$  and  $-2.4760$ , 20.8 and 24.8% lower in magnitude, respectively. The SDQ-MP4 values are close to those obtained with CCSD. The same is observed for MP4 and CCSD(T). The relative magnitude of the Cartesian components of the dipole polarizability shows that the molecule is very anisotropic. Our best values for the mean and the anisotropy are  $\bar{\alpha} = 93.66$  and  $\Delta\alpha = 55.87$

Table 2  
*Ab initio* dipole polarizability for (CdSe)<sub>2</sub>

Method	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\bar{\alpha}$	$\Delta\alpha$
<i>SV0</i>					
SCF	97.97	139.33	148.53	128.61	65.97
MP2	107.36	155.33	167.41	143.37	77.80
SDQ-MP4	106.24	155.66	165.45	142.45	77.75
MP4	109.50	161.17	171.27	147.31	81.16
CCSD	106.05	154.65	164.45	141.72	76.60
CCSD(T)	108.99	159.73	169.16	145.96	79.27
<i>SV1</i>					
SCF	98.06	140.06	150.97	129.70	68.43
MP2	107.76	156.36	169.64	144.59	79.80
<i>SV2</i>					
SCF	97.21	140.38	150.86	129.48	69.66
MP2	107.58	157.27	169.81	144.89	80.62
<i>T0</i>					
SCF	97.01	139.13	147.81	127.99	66.56
MP2	112.05	161.22	172.32	148.53	78.57
SDQ-MP4	112.33	162.62	172.80	149.25	79.31
MP4	114.86	166.89	177.22	152.99	81.87
CCSD	111.68	160.21	171.51	147.80	77.86
CCSD(T)	113.69	163.64	174.93	150.75	79.83
<i>T1</i>					
SCF	96.83	139.60	147.41	127.95	66.71
MP2	106.86	157.87	166.45	143.73	78.91
<i>T2</i>					
SCF	96.53	139.83	148.27	128.21	67.99
MP2	107.10	158.22	167.16	144.16	79.38

Table 3  
*Ab initio* dipole polarizability for (CdSe)<sub>3</sub>

Method	$\alpha_{xx}$	$\alpha_{zz}$	$\bar{\alpha}$	$\Delta\alpha$
<i>SV0</i>				
SCF	131.02	206.39	181.27	−106.59
MP2	141.42	229.27	199.99	−124.24
<i>SV1</i>				
SCF	130.50	207.60	181.90	−109.04
MP2	141.06	230.61	200.76	−126.64
<i>SV2</i>				
SCF	130.35	207.71	181.93	−109.40
MP2	141.62	230.95	201.17	−126.33
<i>T0</i>				
SCF	130.07	207.03	181.38	−108.83
MP2	147.63	237.74	207.70	−127.43
<i>T1</i>				
SCF	129.62	205.06	179.91	−106.70
MP2	140.41	229.00	199.47	−125.29
<i>T2</i>				
SCF	129.27	205.75	180.26	−108.16
MP2	140.55	229.82	200.06	−126.24

(basis set T3). Both sequences of basis sets are close to the reference result of the mean polarizability. The SV sequence predicts a larger anisotropy at the SCF level. The effect of electron correlation is quite small on the longitudinal component but large enough on the transversal one. Consequently, the overall effect leads to a significant

Table 4  
*Ab initio* dipole polarizability for (CdSe)<sub>4</sub>

Method	$\alpha$
<i>SV0</i>	
SCF	219.61
MP2	245.37
<i>SV1</i>	
SCF	220.37
MP2	246.27
<i>SV2</i>	
SCF	220.51
MP2	247.17
<i>T0</i>	
SCF	218.55
MP2	247.52
<i>T1</i>	
SCF	218.46
MP2	244.66
<i>T2</i>	
SCF	219.13
MP2	245.76

Table 5  
B3LYP and B3PW91 dipole moment and polarizability of CdSe

Method	$\mu_z$	$\alpha_{xx} = \alpha_{yy}$	$\alpha_{zz}$	$\bar{\alpha}$	$\Delta\alpha$
<i>SV0</i>					
B3LYP	−2.4772	71.01	114.21	85.41	43.21
B3PW91	−2.6033	70.76	114.15	85.22	43.39
<i>SV1</i>					
B3LYP	−2.4139	70.17	114.33	84.89	44.16
B3PW91	−2.5281	69.96	114.64	84.85	44.68
<i>SV2</i>					
B3LYP	−2.4097	70.64	113.99	85.09	43.35
B3PW91	−2.5265	70.28	114.25	84.94	43.97
<i>T0</i>					
B3LYP	−2.4673	73.76	114.33	87.29	40.56
B3PW91	−2.6000	73.50	113.90	86.96	40.40
<i>T1</i>					
B3LYP	−2.4100	71.35	113.59	85.43	42.24
B3PW91	−2.5302	70.67	113.22	84.85	42.56
<i>T2</i>					
B3LYP	−2.4121	71.38	113.62	85.46	42.24
B3PW91	−2.5323	70.78	113.32	84.96	42.54

increase of the mean and a decrease of the anisotropy. At the CCSD(T)/T2 level of theory  $\bar{\alpha} = 102.15$  and  $\Delta\alpha = 40.74$ , an increase of 9.1 and a decrease of 27.07%, respectively.

The B3PW91 method predicts a dipole moment systematically larger in magnitude than the B3LYP one. For the mean and the anisotropy of the polarizability both methods predict values in close agreement. Compared to the conventional *ab initio* methods, both DFT ones yield values very close to the most accurate CCSD and CCSD(T). This is hardly the case with the dipole polarizability. Both methods underestimate significantly the components of the

Table 6  
B3LYP and B3PW91 polarizability of (CdSe)<sub>2</sub>

Method	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\bar{\alpha}$	$\Delta\alpha$
<i>SV0</i>					
B3LYP	101.97	148.55	172.73	141.08	88.10
B3PW91	101.23	147.76	168.12	139.04	83.99
<i>SV1</i>					
B3LYP	102.10	149.15	175.40	142.21	90.97
B3PW91	101.15	148.30	170.72	140.05	86.98
<i>SV2</i>					
B3LYP	98.34	149.54	175.28	141.05	95.94
B3PW91	97.28	148.73	167.95	137.99	89.50
<i>T0</i>					
B3LYP	101.35	149.61	169.58	140.18	85.93
B3PW91	101.06	148.12	164.67	137.95	80.84
<i>T1</i>					
B3LYP	100.18	149.71	170.35	140.08	88.33
B3PW91	99.29	148.46	165.77	137.84	84.48
<i>T2</i>					
B3LYP	100.41	149.81	170.83	140.35	88.54
B3PW91	99.27	148.71	166.51	138.16	85.34

Table 7  
B3LYP and B3PW91 polarizability of (CdSe)<sub>3</sub>

Methods	$\alpha_{xx}$	$\alpha_{zz}$	$\bar{\alpha}$	$\Delta\alpha$
<i>SV0</i>				
B3LYP	135.37	235.00	201.62	−140.54
B3PW91	134.32	230.15	198.21	−135.52
<i>SV1</i>				
B3LYP	135.05	235.73	202.17	−142.38
B3PW91	133.91	231.35	198.87	−137.80
<i>SV2</i>				
B3LYP	135.13	235.53	202.06	−141.98
B3PW91	133.85	231.32	198.83	−137.84
<i>T0</i>				
B3LYP	134.50	232.42	199.78	−138.49
B3PW91	134.10	227.67	196.48	−132.32
<i>T1</i>				
B3LYP	133.02	232.21	199.15	−140.29
B3PW91	131.95	227.56	195.69	−135.22
<i>T2</i>				
B3LYP	133.58	232.58	199.58	−140.01
B3PW91	132.11	228.20	196.17	−135.90

polarizability. This results in a systematic underestimation of the mean polarizability.

(CdSe)<sub>2</sub>. The largest basis sets predict the following SCF values:  $\bar{\alpha} = 129.48$ (SV2), 128.21 (T2) and  $\Delta\alpha = 69.66$  (SV2), 67.99 (T2). The mean values agree quite well but the SV2 basis predicts a larger anisotropy. The SV0 post-Hartree–Fock calculations show that electron correlation increases the magnitude of all components of the polarizability. The CCSD(T)/SV0 values  $\bar{\alpha} = 145.96$  and  $\Delta\alpha = 79.27$ , are 13.5% and 20.2% above the respective SCF values. Similar results are obtained with the T0 basis. It is interesting to observe that for the dimer the

Table 8  
B3LYP and B3PW91 polarizability of (CdSe)<sub>4</sub>

Method	$\alpha$
SV0	
B3LYP	247.73
B3PW91	243.63
SV2	
B3LYP	248.57
B3PW91	244.43
T0	
B3LYP	245.08
B3PW91	240.97
T1	
B3LYP	245.31
B3PW91	241.14
T2	
B3LYP	246.03
B3PW91	242.08

MP2 method is quite close to the most accurate CCSD and CCSD(T). This is a significant change over the monomer.

We observe that mean and anisotropy values calculated with B3LYP are systematically larger than those obtained with the B3PW91 method. Both methods predict mean values close to the *ab initio* ones but the anisotropies are larger.

(CdSe)<sub>3</sub>. All basis sets yield mean polarizability values very close to SV2 and T2. It is remarkable that the good agreement extends to the anisotropy as well. We have obtained MP2 values with all basis sets. In all cases electron correlation enhances the magnitude of the Cartesian components. Our best values are obtained with the T2 basis and are  $\bar{\alpha} = 200.06$  and  $\Delta\alpha = -126.24$ . The increase in magnitude is 11.0% and 16.7%, respectively.

Again, the mean and the anisotropy obtained with B3LYP are larger in magnitude than the B3PW91 ones. Compared to MP2, B3LYP and B3PW91 predict reasonable values for the mean but larger in magnitude for the anisotropy.

(CdSe)<sub>4</sub>. For this isotropic system all basis sets predict SCF values quite close to the  $\alpha = 220.51$  (SV2) and 219.13 (T2). The respective MP2 values are 247.17 (SV2) and 245.76 (T2). The observed enhancement is 12.1 and 12.2%, respectively.

It is interesting to note again that the order  $\alpha(\text{B3LYP}) > \alpha(\text{B3PW91})$  is observed for the tetramer as well. The values of both methods are somewhat lower than the MP2 ones.

**Final remarks.** In Fig. 5 we have traced the evolution of the mean polarizability per atom obtained with basis set SV2 for the methods SCF, MP2 and B3LYP. The overall picture is very close to that previously reported [10]. We

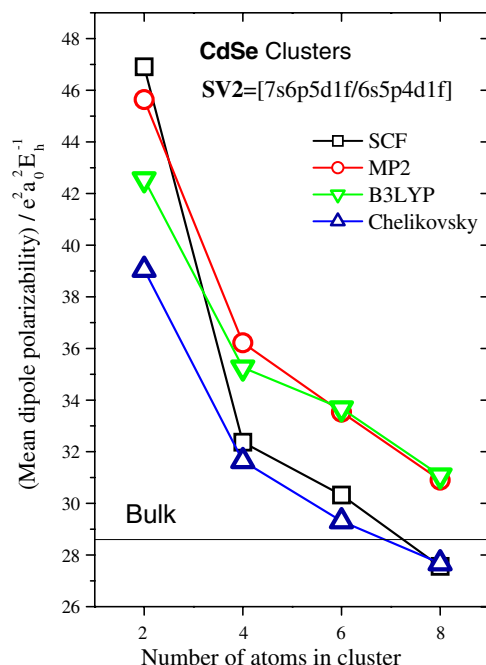


Fig. 5. Evolution of the mean polarizability per atom in (CdSe)<sub>n</sub>,  $n = 1-4$ .

see that our MP2 and B3LYP values converge with increasing cluster size. The results obtained by Troparevsky and Chelikowsky [7] are closer to our SCF ones. It is easily seen

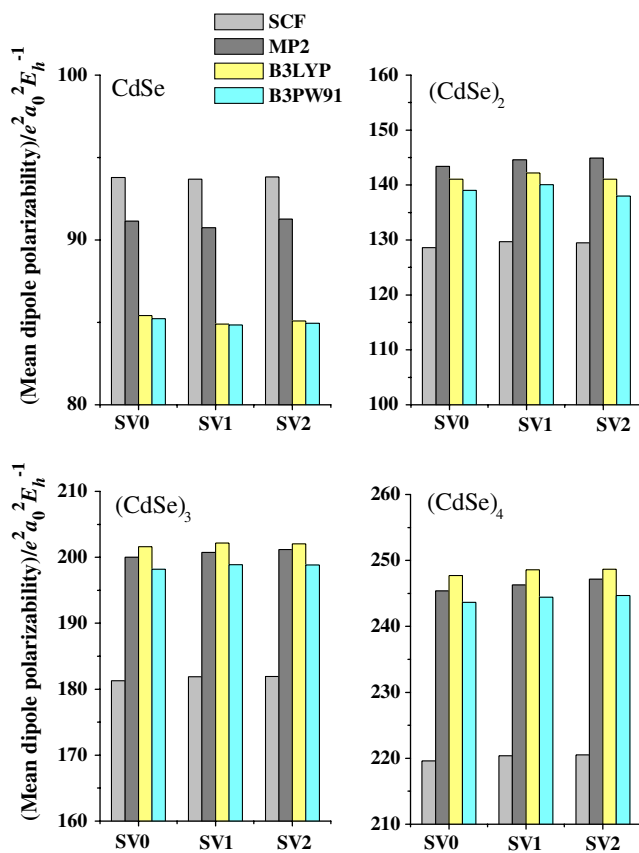


Fig. 6. Comparative performance of the SV0, SV1 and SV2 basis sets on (CdSe)<sub>n</sub>,  $n = 1-4$ .



that theory predicts a fast convergence to the bulk value of the polarizability [11].

In Fig. 6 we offer an aperçu of the comparative performance of the SV0, SV1 and SV2 basis sets on  $(\text{CdSe})_n$ ,  $n = 1, 2, 3$  and 4. It is easily seen that the small sized SV0 basis set could easily be chosen for calculations on larger clusters. The MP2 methods should be expected to provide an accurate picture of the polarizability in these systems. The B3LYP and B3PW91 should provide acceptable mean polarizabilities.

#### 4. Conclusions, perspectives and work in progress

We have reported a systematic study of the polarizability of small cadmium selenide clusters. We have analyzed basis set effects for all molecules. A systematic divergence is observed between the B3LYP and B3PW91 methods with increasing cluster size. We propose a MP2/SV0 strategy for the calculation of the electric polarizability of middle-sized cadmium selenide clusters. B3LYP/SV0 and B3PW91/SV0 should be expected to predict mean polarizabilities only a few percent different than MP2/SV0 but the performance should not be equally good for the anisotropy.

Work is now in progress for the extension of polarizability calculations to larger cadmium selenide clusters. Much of the success of this effort will depend on the applicability of high-level computational methods to clusters  $(\text{CdSe})_n$  with  $n \geq 6$ . In recent work we applied a class of DFT-based methods to challenging problems, as the calculation of the polarizability and hyperpolarizability of ozone [15] and the lithium tetramer [16]. We used a metric approach and pattern recognition techniques in order to analyze the similarity and relative merit of DFT methods [33]. A similar study on  $(\text{CdSe})_n$ ,  $n \leq 4$ , currently in progress, will enable us to define reliable strategies for the extension of our efforts to large CdSe clusters.

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