Theor Chem Acc (2000) 104:189–194
DOI 10.1007/s002140000134

Theoretical
Chemistry Accounts

Regular article

An ab initio multireference doubles excitation configuration interaction study of low-lying electronic states of Cd_2 using Slater-type orbitals

José M. García de la Vega[1], **Beatriz Miguel**[1,2]

[1] Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain
[2] Departamento de Química Física, Universidad de Murcia, 30100 Murcia, Spain

Received: 16 September 1999 / Accepted: 3 February 2000

Abstract. Potential-energy curves for the ground state and lower excited states of the Cd_2 dimer have been calculated. They are obtained using a multireference doubles excitation configuration interaction procedure and employing Slater basis sets, previously optimized at the self-consistent-field level for excited states of the Cd atom. The spectroscopic constants and excitation energies for the bound states of Cd_2 have been compared with experimental as well as other theoretical results. The ground state of Cd_2 is essentially repulsive and presents a shallow van der Waals minimum. The computed adiabatic electronic transitions are in good agreement with the experimental ones.

Keywords: Excited states – Slater-type orbital basis set – Electronic spectra small clusters

1 Introduction

Basis sets are typically optimized for the ground state of neutral atoms; however, the atomic state of the metal atom in transition-metal compounds often corresponds to higher energy configurations [1]. The Cd atom has the closed-shell configuration [Kr] $4d^{10}5s^2$. Only weak, van der Waals binding is expected for the interaction of ground-state cadmiun atoms (^1S). On the other hand, excited states of the Cd_2 molecule, coming from the states $^1S + {}^3P$ and $^1S + {}^1P$ of separated atoms, may be bound by a substantial amount of energy, at bound distances which are considerably smaller than those of the ground states. The Cd_2 molecule is of considerable interest in its application in possible high-power visible and UV lasers, so the excited states of Cd_2 include many interesting problems.

A large number of experiments on the absorption and emission spectra were performed for cadmium vapor around the 1930s [2]. Several authors [3–6] have assigned the electronic transitions to the $X(^1\Sigma_g^+) \rightarrow A(^1\Sigma_u^+)$ transition of Cd_2. Vreede et al. [7] also observed a green fluorescence attributed to the $(^3\Sigma_u^+) \rightarrow X(^1\Sigma_g^+)$ transition and Kowalski et al. [8] detected the transition $(^3\Pi_u) \rightarrow X(^1\Sigma_g^+)$ in laser-induced fluorescence. Stevens [9] found that the lowest excited level was $^3\Pi_g$, a metastable state that acts as a reservoir for excitation energy, showing charge transfer at 470 nm from this state to the bound $^3\Pi_u$ state. Su et al. [10] obtained spectroscopic constants for Cd_2 from its absorption spectrum.

More recently, Czajkowski et al. [11] studied the excitation spectrum of Cd_2, produced in a free-jet molecular beam crossed with a pulsed dye-laser beam. They obtained well-resolved structures arising from transitions between the vibrational levels of the X $(^1\Sigma_g^+)$ and $(^3\Pi_u)$ states. They also gave the vibrational constants and bond strengths of the molecule in both electronic states. The bound-free decay of the $^1\Sigma_u^+$ state was investigated from the fluorescence observed in the 222–227 nm region by Rodriguez and Eden [12].

A few ab initio calculations on the Cd_2 dimer have appeared. Bender et al. [13] performed configuration interaction (CI) calculations with the four valence electrons of Cd_2, working with Gaussian basis sets, for the ground state and eight low-lying excited states. Multiconfigurational self-consistent-field (SCF) calculations on this system were carried out by Stevens [9]. More recently Czuchaj et al. [14] computed potential-energy curves for a number of electronic states of this dimer, using the multireference doubles excitation CI [MRDCI(SD)] method for the valence electrons and pseudopotentials for the core electrons. Their potential curves for the ground-state $^1\Sigma_g^+$ state exhibited a shallow van der Waals minimum as the same authors found in the ab initio calculations of Zn_2.

Despite the existence of these ab initio calculations on the Cd dimers there is still a demand for more accurate

---

Correspondence to: J. M. García de la Vega potentials for these species. The existing potentials prove to be inadequate for an explanation of the findings supplied by more and more sophisticated experiments. Encouraged by our previous calculations on the excited states of transition metals [1, 15], we decided to perform MRDCI calculations on the Cd_2 dimer using Slater-type functions (STFs). The potential advantages of STFs over the widely used Gaussian-type functions (GTFs) are well known [16]; however, most molecular calculations are carried out with GTF basis sets due to the difficulties involved in the calculation of many-center integrals with STFs. Moreover, it is well known that electron correlation effects are extremely important in transition-metal systems. We report the results of MRDCI calculations on the lower electronic states of Cd_2 using STFs that hopefully will be useful for a better understanding of the heavier atom dimers.

2 Optimized STFs and calculations for excited states of the Cd atom

The first excited configuration of the Cd atom, [Kr] $4d^{10}5s^{1}4p^{1}$, gives two electronic states, ^{3}P and ^{1}P. In order to improve the description of the *p* orbitals two 5*p* functions were added to the original double-zeta (DZ) basis sets [18] for the ground state (^{1}S). All the exponents of the new augmented basis sets were optimized with respect to the atomic SCF energy of the ^{3}P or ^{1}P states, separately. The new optimized basis sets for the ^{3}P (DZ/3P) and ^{1}P (DZ/1P) states are given in Table 1. The corresponding energies and virial ratios obtained for the ^{3}P and ^{1}P states of the Cd atom are also shown in Table 1. The energy optimizations were carried out with a modification of the atomic SCF program of Pitzer [17], maintaining the atomic symmetry.

Table 1. Exponents, energies (hartrees) and virial ratios for double-zeta (*DZ*) optimized basis sets for the ^{3}P and ^{1}P states of the Cd atom. The energy and virial ratio of the DZ basis set [31] for the ^{1}S state are −5465.09805272 hartrees and −2.00000000, respectively

DZ/3P		DZ/1P	
1*s*	49.227269	1*s*	49.226209
1*s*	33.881060	1*s*	33.872110
2*s*	22.151231	2*s*	22.112439
2*s*	21.831134	2*s*	21.836148
3*s*	15.895054	3*s*	15.972703
3*s*	10.463284	3*s*	10.459764
4*s*	6.0226882	4*s*	6.0013745
4*s*	4.0603002	4*s*	4.0311115
5*s*	2.3610834	5*s*	2.2148258
5*s*	1.3489503	5*s*	1.1765725
2*p*	31.005515	2*p*	31.021135
2*p*	20.388321	2*p*	20.392409
3*p*	10.827932	3*p*	10.824481
3*p*	7.1501391	3*p*	7.0921040
4*p*	6.1516883	4*p*	6.1968888
4*p*	3.8409267	4*p*	3.8716726
5*p*	1.9561589	5*p*	2.0364131
5*p*	1.0562350	5*p*	1.1582798
3*d*	16.671252	3*d*	16.675998
3*d*	9.5158200	3*d*	9.5180839
4*d*	5.2119911	4*d*	5.2183957
4*d*	2.7151628	4*d*	2.7238662
E	−5465.02024101	*E*	−5464.93926421
V	−1.99999955	*V*	−1.99999944

CI calculations were carried out with the MRDCI method of Buenker and Phillips [19–21] with an adapted Slater integral program [22], which was recently applied with success to light homonuclear diatomic molecules [15, 23]. Some of the occupied atomic orbitals (AOs) were frozen in the MRDCI calculation, particularly the nine occupied AOs corresponding to the 1*s*, 2*s*, 2*p*, 3*s* and 3*p* inner shells. The rest of the occupied and virtual AOs were used in the MRDCI calculations for the ^{1}S, ^{3}P and ^{1}P states of the Cd atom. The number of reference configurations was selected so that a Geisser coefficient (C^2) higher than or equal to 0.94 was obtained. The selection threshold for the energy was 10 μhartrees. The number of configuration functions generated (symmetric adapted functions total, SAFT) and of those selected for the final approximate full CI are given in Table 2. Extrapolation of the energy to zero threshold gives the MRDCI energy. Finally, we used the multireference correction [24] (analogous to the Davidson correction [25]) to obtain the full CI extrapolated energy. These MRDCI and full CI energies, also shown in Table 2, are lower than those obtained in the more accurate calculations with GTFs. Calculations with the DZ and the limiting Hartree–Fock (LHF) basis set of Clementi and Roetti [18] show that several intruder excited states (^{3}S and the second ^{1}S and ^{3}S, third ^{3}S, ^{1}D and ^{3}D) give lower energies than the ^{3}P and ^{1}P states of Cd, which are placed at energies above 56 eV the ^{1}S ground state for the DZ basis set and 19 eV for the LHF basis set. Clearly, the basis sets previously optimized for the ground states of the Cd atom produce a bad description of the atomic excited states. They give a better description of S and D states than P states since the 5*s* and 4*d* are valence shell orbitals, being represented by diffuse STFs that would better reproduce the virtual *s* and *d* orbitals. Nevertheless the inner 4*p* STFs, which are more concentrated functions since they reproduce orbitals from the inner shell, are not satisfactory to describe the excited P states. Indirectly, in the optimization of the DZ/3P and DZ/1P basis sets the optimization of the 5*p* occupied shell led to an indirect optimization of the *p* virtual AOs, allowing less energetic excitations with P symmetry. As shown previously for the Zn atom [15] and for the Cd atom here, the inclusion of correlation in these DZ basis sets cannot correct this effect.

The computed and experimental [26] excitation energies for the neutral, cationic and anionic Cd, as well as the ionization potentials (IP) and electron affinities (EA) are presented in Table 3. Optimized DZ basis sets give excitation energies for ^{3}P and ^{1}P that are in good agreement with the experimental values. Also the value for the energy excitation from the ^{2}S to the ^{2}P state of the cation is reasonable; however it is clear that for the higher excited states a new improvement of the basis sets would be required. As mentioned previously DZ and LHF basis sets do not give satisfactory excitation energies for the ^{3}P and ^{1}P states of the Cd atom or the

Table 2. Multireference doubles excitation configuration interaction (*MRDCI*) and extrapolated energies (hartrees) for the ground state and low-lying excited states of the Cd atom

Basis set	State	Symmetric adapted functions total	Symmetric adapted functions	MRDCI	C^2	Extrapolated CI
DZ	^{1}S	910386	25655	−5465.4201	0.98	−5465.4277
	^{3}S	1487661	25251	−5465.1369	0.98	−5465.1437
	(2)^{1}S	910386	25655	−5465.0771	0.98	−5465.0854
	(2)^{3}S	1487661	25251	−5464.2582	0.98	−5464.2656
	(3)^{1}S	910386	25655	−5464.2193	0.96	−5464.2317
	^{3}P	1487661	25251	−5463.2770	0.97	−5463.2893
	^{1}P	910386	25655	−5463.2337	0.95	−5463.2526
DZ/3P	^{1}S	1782165	37293	−5465.4461	0.95	−5465.4631
	^{3}P	2974713	35230	−5465.3450	0.98	−5465.3527
	^{1}P	1782165	37293	−5465.2597	0.97	−5465.2705
DZ/1P	^{1}S	1782165	38013	−5465.4464	0.95	−5465.4634
	^{3}P	2974713	31469	−5465.3459	0.98	−5465.3535
	^{1}P	1782165	38013	−5465.2508	0.97	−5465.2616
Limiting Hartree−Fock	^{1}S	1759586	26248	−5465.4303	0.98	−5465.4422
	^{3}S	2878301	25829	−5465.2338	0.97	−5465.2434
	(2)^{1}S	1759586	26248	−5465.2103	0.96	−5465.2232
	(2)^{3}S	2878301	25829	−5465.0055	0.97	−5465.0172
	(3)^{1}S	1759586	26248	−5464.9782	0.96	−5464.9914
	^{3}P	2878301	25829	−5464.7138	0.96	−5464.7281
	^{1}P	1759586	26248	−5464.6290	0.94	−5464.6531

Table 3. Excitation energies, ionization potential and electron affinity (eV) for Cd, Cd^+ and Cd^-

State		ΔE (eV)				
		DZ/3P	DZ/1P	DZ	Limiting Hartree–Fock	Exp.[a]
Cd $4d^{10}$ $5s^2$	^{1}S	0.00	0.00	0.00	0.00	0.00
Cd $4d^{10}$ $5s^1$ $5p^1$	^{3}P	3.01	2.99	58.2	19.4	3.83
Cd $4d^{10}$ $5s^1$ $5p^1$	^{1}P	5.24	5.49	59.2	21.5	5.42
Cd $4d^{10}$ $5s^1$ $6s^1$	^{3}S	8.62	7.36	7.73	5.41	6.38
Cd $4d^{10}$ $5s^1$ $6s^1$	^{1}S	9.67	8.46	9.31	5.96	6.61
Cd^+ $4d^{10}$ $5s^1$	^{2}S	0.00	0.00	0.00	0.00	0.00
Cd^+ $4d^{10}$ $5p^1$	^{2}P	4.98	4.83	57.3	19.5	5.63
Cd^+ $4d^9$ $5s^2$	^{2}D	10.3	10.2	11.2	10.7	8.94
Cd^- $4d^{10}$ $5s^2$ $5p^1$	^{2}P	0.00	0.00	0.00	0.00	
Cd^- $4d^{10}$ $5s^2$ $6s^1$	^{2}S	5.21	3.48	−52.5	−17.8	
Ionization potential		7.72	7.79	7.01	7.44	8.99
Electron affinity		−1.42	−1.61	−6.74[b] −59.3[c]	−2.03[b] −19.8[c]	

[a] Ref. [26]

[b] With respect to the ^{2}S Cd^-ground state obtained in the calculation

[c] With respect to the ^{2}P Cd^- ground state

^{2}P state of the cation. In the case of the anion the relative order between the energies of the ^{2}P ground state and ^{2}S first excited state is reversed, the ^{2}S state being more stable by 52.5 and 17.8 eV for DZ and LHF basis sets, respectively. The IP are well described by the four basis sets, as expected because the ground states of both atom and cation do not concern 5*p* orbitals. However the EA varies significantly with the basis set, since the ground state of the anion is $4d^{10}$ $5s^2$ $5p^1$ (^{2}P), (i.e., it has an electron in the 5*p* shell, so we could expect that the EA value will be close to −1.4 or −1.6 eV.

Finally estimated the basis set superposition error (BSSE) in the present calculations. Following the idea of Boys and Bernardi [27] we found that the BSSE varies between a minimum value of 0.0013 hartrees for $R = 8.0$ Å and a maximum value of 0.0054 hartrees for $R = 2.30$ Å. The curves presented in this work were corrected by taking these BSSE corrections into account.

3 MRDCI potential-energy curves of Cd_2

The calculations described in this study were made with a Slater molecular integral program [22] adapted to the MRDCI code [19–21]. This coupling of codes allows us to use the D_{2h} symmetry group, as a subgroup of $D_{\infty h}$, in the calculations. The lowest 36 occupied molecular orbitals (MOs) and the highest 24 virtual MOs are discarded in the generation of all the SAFT. The reference configurations used for the singlet and triplet states remain constant through all the internuclear (R) range and they are summarized in Table 4, grouped by symmetry. They were selected to achieve a Geisser coefficient higher than 0.93 in all the calculated points, with a threshold in the energy of 10 μhartrees.

The roots corresponding to the ground state and the eight low-lying excited states (four states are singlets and four triplets) were computed. In these calculations we used the DZ/3P basis set (Table 1), taking into account the results obtained in the atomic excitations.

The MRDCI energy curves for Cd_2 are shown in Fig. 1. In general, these results agree with those previously reported [13, 14]. The ${}^1\Sigma_g^+$, ground state formed by two Cd atoms in the ${}^1S$ state, is essentially repulsive, with a shallow van der Waals minimum. Among the potential-energy curves calculated for the triplet states, that dissociate into Cd (${}^3P$) + Cd (${}^1S$), we found two states with a well-defined depth (${}^3\Pi_g$ and ${}^3\Sigma_u^+$) and a repulsive state (${}^3\Sigma_g^+$). The fourth triplet state, ${}^3\Pi_u$, has a small minimum. On the other hand, all the singlet states, which dissociate into Cd (${}^1P$) + Cd (${}^1S$), are bound states. Our potential curves are qualitatively similar to those of Bender et al. [13] and Czuchaj et al. [14], but there are some discrepancies. First, the potential curves in the work of Czuchaj et al. [14] were shifted to achieve the energies of the Cd ${}^3P$ state (3.83 eV) and the Cd ${}^1P$ state (5.42 eV) in the dissociation limit of Cd_2. The unshifted curves of Bender et al. [13] give slightly lower values for these energies, 2.92 eV (${}^3P$) and 5.18 eV (${}^1P$), similar to our values of 3.01 and 5.24 eV, respectively. Obviously this shift can modify the relative R values where the different states cross, and the values of the atomic dissociations are a test of the behavior of both the basis set employed and the computational method. We obtained the crossing of the ${}^3\Pi_g$ and ${}^3\Sigma_u^+$ states at 3.0 Å, while in Refs. [13, 14] it appears at 3.4 Å, outside

Table 4. Reference configurations for the MRDCI calculations of singlet and triplet states of Cd_2

Σ_g^+	Σ_u^+	Π_g	Π_u
Singlet and triplet states			
$10\sigma_g^2\ 10\sigma_u^1\ 11\sigma_u^1$	$10\sigma_g^2\ 10\sigma_u^1\ 11\sigma_g^1$	$10\sigma_g^2\ 10\sigma_u^1\ 6\pi_u^1$	$10\sigma_g^2\ 10\sigma_u^1\ 6\pi_g^1$
$10\sigma_u^1\ 11\sigma_u^1\ 11\sigma_g^2$	$10\sigma_u^1\ 11\sigma_g^1\ 11\sigma_u^2$	$10\sigma_u^1\ 11\sigma_g^2\ 6\pi_u^1$	$10\sigma_u^1\ 11\sigma_g^2\ 6\pi_g^1$
$10\sigma_u^1\ 11\sigma_u^1\ 6\pi_u^2$	$10\sigma_u^1\ 11\sigma_g^1\ 6\pi_u^2$	$10\sigma_u^1\ 6\pi_u^3$	$10\sigma_u^1\ 6\pi_u^2\ 6\pi_g^1$
$10\sigma_u^1\ 11\sigma_u^1\ 6\pi_g^2$	$10\sigma_u^1\ 11\sigma_g^1\ 6\pi_g^2$	$10\sigma_u^1\ 6\pi_u^1\ 6\pi_g^2$	$10\sigma_u^1\ 6\pi_g^3$
$10\sigma_g^1\ 10\sigma_u^2\ 11\sigma_g^1$	$10\sigma_g^1\ 10\sigma_u^2\ 11\sigma_u^1$	$10\sigma_g^1\ 11\sigma_g^2\ 6\pi_g^1$	$10\sigma_g^1\ 11\sigma_g^2\ 6\pi_u^1$
$10\sigma_g^1\ 10\sigma_u^2\ 12\sigma_g^1$	$10\sigma_g^1\ 11\sigma_g^2\ 11\sigma_u^1$	$10\sigma_g^1\ 6\pi_u^2\ 6\pi_g^1$	$10\sigma_g^1\ 6\pi_u^3$
$5\pi_u^3 \cdots 10\sigma_g^2\ 10\sigma_u^2\ 6\pi_u^1$	$10\sigma_g^1\ 11\sigma_u^1\ 6\pi_u^2$	$10\sigma_g^1\ 10\sigma_u^2\ 6\pi_g^1$	$10\sigma_g^1\ 10\sigma_u^2\ 6\pi_u^1$
$5\pi_g^3 \cdots 10\sigma_g^2\ 10\sigma_u^2\ 6\pi_g^1$	$10\sigma_g^1\ 11\sigma_u^1\ 6\pi_g^2$	$10\sigma_g^1\ 6\pi_g^3$	$10\sigma_g^1\ 6\pi_u^1\ 6\pi_g^2$
$9\sigma_u^1 \cdots 10\sigma_g^2\ 10\sigma_u^2\ 11\sigma_u^1$	$10\sigma_g^1\ 10\sigma_u^1\ 11\sigma_g^2$	$10\sigma_g^2\ 11\sigma_g^1\ 6\pi_g^1$	$10\sigma_g^2\ 11\sigma_g^1\ 6\pi_u^1$
$2\delta_u^3 \cdots 10\sigma_g^2\ 10\sigma_u^2\ 11\sigma_u^1$	$10\sigma_g^1\ 10\sigma_u^1\ 11\sigma_u^2$	$11\sigma_g^1\ 6\pi_u^2\ 6\pi_g^1$	$11\sigma_g^1\ 6\pi_u^3$
$10\sigma_g^1\ 10\sigma_u^1\ 6\pi_u^1\ 6\pi_g^1$	$10\sigma_g^1\ 10\sigma_u^1\ 6\pi_u^2$	$10\sigma_u^2\ 11\sigma_g^1\ 6\pi_g^1$	$10\sigma_u^2\ 11\sigma_g^1\ 6\pi_u^1$
	$10\sigma_g^1\ 10\sigma_u^1\ 6\pi_g^2$	$11\sigma_g^1\ 6\pi_g^3$	$11\sigma_g^1\ 6\pi_u^1\ 6\pi_g^2$
	$10\sigma_g^2\ 10\sigma_u^1\ 12\sigma_g^1$	$10\sigma_g^1\ 10\sigma_u^1\ 11\sigma_g^1\ 6\pi_u^1$	$10\sigma_g^1\ 10\sigma_u^1\ 11\sigma_g^1\ 6\pi_g^1$
	$10\sigma_u^1\ 11\sigma_g^2\ 12\sigma_g^1$		
	$10\sigma_g^2\ 11\sigma_g^1\ 11\sigma_u^1$		
	$10\sigma_g^2\ 6\pi_u^1\ 6\pi_g^1$		
Singlet states			
$10\sigma_g^2\ 10\sigma_u^2$	$10\sigma_g^2\ 10\sigma_u^1\ 13\sigma_g^1$		
$10\sigma_u^2\ 11\sigma_g^2$	$10\sigma_g^1\ 11\sigma_g^1\ 6\pi_u^1\ 6\pi_g^1$		
$10\sigma_u^2\ 6\pi_u^2$			
$10\sigma_u^2\ 6\pi_g^2$			
$10\sigma_g^2\ 11\sigma_g^2$			
$10\sigma_g^2\ 6\pi_u^2$			
$10\sigma_g^2\ 6\pi_g^2$			
$10\sigma_g^1\ 10\sigma_u^1\ 11\sigma_g^1\ 11\sigma_u^1$			
Triplet states			
$10\sigma_g^1\ 11\sigma_g^1\ 6\pi_u^2$	$10\sigma_u^2\ 6\pi_u^1\ 6\pi_g^1$	$10\sigma_g^2\ 11\sigma_u^1\ 6\pi_u^1$	$10\sigma_g^2\ 11\sigma_u^1\ 6\pi_g^1$
$10\sigma_g^1\ 11\sigma_g^1\ 6\pi_g^2$			
$10\sigma_g^1\ 10\sigma_u^2\ 13\sigma_g^1$			
$10\sigma_g^2\ 10\sigma_u^1\ 12\sigma_u^1$			
$10\sigma_g^2\ 10\sigma_u^1\ 13\sigma_u^1$			
$10\sigma_g^2\ 11\sigma_g^1\ 12\sigma_g^1$			
$10\sigma_g^2\ 11\sigma_g^1\ 13\sigma_g^1$			

the minimum region of both states. The rest of our crossing description agrees with the results of Bender et al. For example, the threefold crossing of the $^3\Sigma_g^+$, $^1\Sigma_u^+$ and $^1\Pi_u$ states appears around 3.16 Åin Ref. [13] and at 3.05 Å in the present results, while in Ref. [14] only the $^3\Sigma_g^+$ and $^1\Sigma_u^+$ states cross around 3.3 Å. Also the crossing between the $^3\Sigma_g^+$ and $^1\Sigma_g^+$ states occurs in Ref. [13] and Fig. 1 at $R \simeq 3.0$ Å, and the crossing between $^1\Pi_g$ and $^3\Sigma_g^+$ states in the three calculations occurs at R $\simeq$ 3.6 Å. In general, the details of the description of the singlet excited states in Ref. [14] do not agree with the results of Bender et al. [13] and the ones presented here. In spite of the $^1\Pi_g$ and $^1\Sigma_u^+$ being similarly placed with respect to the triplet states, the $^1\Pi_u$ and $^1\Sigma_g^+$ states are considerably separated from the $^1\Pi_g$ and $^1\Sigma_u^+$ states and only cross with them at $R \leq 1.5$ Å.

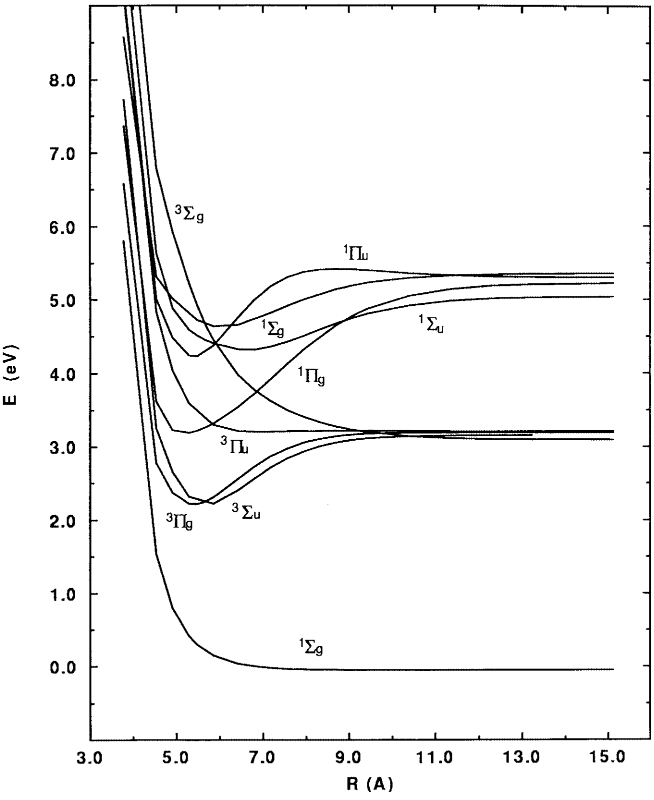

Fig. 1. Multireference doubles excitation configuration interaction potential-energy curves for Cd_2 using a DZ/3P basis set

Another difference in the appearance of the Cd_2 potential curves is the hump of the $^1\Pi_u$ state, which appears at $R \simeq 4.5$ Å (Fig. 1) with an energy barrier of about 0.14 eV, while this hump is found at 3.77 Å and 5.0 Å in Ref. [14] and Ref. [13], respectively, with barrier heights of 0.35 and 0.12 eV. This hump, that also appears in the Zn_2 molecule [15], has been assigned to the avoided curve-crossing with the cation and anion $^1\Pi_u$ state.

The spectroscopic constants (dissociation energies, bond lengths and vibrational frequencies) obtained in this work are compared with those theoretically [13, 14] and experimentally [11, 12] determined previously in Table 5. Our bond lengths are in good agreement with those of Bender et al. Compared with the results of Czuchaj et al., we find that the bond length differences are larger for the $^1\Sigma_u^+$ and $^3\Pi_u$ states, where our R_e are 0.46 longer and 1.18 Å shorter, respectively. For the $^1\Sigma_g^+$ state our R_e and that of Czuchaj et al. only differ by 0.16 Å, however, compared with the experimental result of Ref. [11] we found that they are 0.9 and 0.7 Å shorter, respectively. For the $^3\Pi_u$ state both results differ and they are shorter than the experimental result, but the value of Czuchaj et al. is closer to it than our result.

The binding energy of the ground state was estimated from the potential-energy curve to be $D_e = 0.060$ eV at $R_e = 4.24$ Å. It must be pointed out that this dissociation energy is not of a comparable magnitude to the computational error (3×10^{-5} eV), but it is comparable to the magnitude of the BSSE error (0.07 eV), so it is important to include this correction.

Most measurements of the continuum absorptions and emissions observed in Cd_2 were made in the 1930s [2]. The binding energy of Cd_2 was first estimated by Winans [28] as $D_0^0(Cd_2) = 0.20$ eV from the energy difference of a Cd resonance line and the short-wave-length limit of the continuum absorption of Cd_2. With a similar method Hamada [29] estimated it as 0.24 eV. By viscosity measurements of Cd vapor, Carlson and Kuschmir [30] obtained $D_0^0(Cd_2) = 0.095 \pm 0.009$ eV at

Table 5. Spectroscopic constants: bond lengths (Å), dissociation energies (eV) and vibrational frequencies (cm^{-1}) at the minima in the CI potential curves of singlet and triplet excited states of Cd_2

State	This work			Ref. [13]			Ref. [14]		Exp.		
	R_e	D_e	ω_e	R_e	D_e	ω_e	R_e	D_e	R$_e$	D_e	ω_e
$^1\Sigma_g^+$	4.24	0.060	18	–	–	–	4.4	0.039	5.10[a]	0.040	22.5
$2^1\Sigma_g^+$	3.17	0.73	124	3.29	0.72	77	–	–			
$^1\Sigma_u^+$	3.46	0.96	94	3.24	0.96	78	3.0	0.96	4.18[b]	1.023	92
$^1\Pi_u$	2.86	1.12	236	2.95	1.02	119	–	–			
$^1\Pi_g$	2.81	2.16	158	2.84	2.17	137	2.7	1.92			
$^3\Sigma_u^+$	3.00	1.13	186	3.06	0.70	104	2.9	0.84			
$^3\Pi_g$	2.82	1.09	192	2.91	0.80	116	2.7	1.04			
$^3\Pi_u$	3.52	0.066	58	–	–	–	4.7	0.031	5.4[a]	0.032	

[a] Ref. [11]
[b] Ref. [12]

Table 6. Adiabatic electronic transitions (nm)

Transition	Exp.	This work
${}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$	222–227[a] 273–279[b]	286
${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$	545[c]	566
${}^3\Pi_u \rightarrow {}^1\Sigma_g^+$	324–326[d]	385

[a] Ref. [12]
[b] Ref. [4]
[c] Ref. [7]
[d] Ref. [8]

$R_e = 3.02 \pm 0.08$ Å. Also experimental data of R_e and D_e were obtained from the temperature dependence of the Cd_2 absorption spectrum by Su et al. [10]: $R_e = 4.82$ Å and $D_e = 0.0475$ eV. Kowalski et al. [8] used an extrapolation of vibronic bands observed in the laser-induced fluorescence spectrum of jet-cooled Cd_2 to obtain reliable $D_0^0(Cd_2) = 0.0378$ eV. The most recent experimental value was determined by Czajkowski et al. [11] from the analysis of the spectra, yielding $R_e = 5.10$ Å and $D_e = 0.040$ eV, and the results are included in Table 5.

Finally, experimental electronic transitions for the Cd_2 molecule and those obtained from the adiabatic transitions between the potential curves are summarized in Table 6. Our results are in good agreement with the experimental ones.

4 Conclusion

The atomic DZ/3P Slater basis set, optimized at the SCF level for the ${}^3P$ state, has been employed within the framework of MRDCI calculations to compute potential-energy curves for low-lying electronic states of Cd_2. The results produce lower energies than those obtained with sophisticated Gaussian basis sets. Additionally, the features of the curves and excitation energies are well reproduced.

Acknowledgement. This work has been supported by Dirección General de Investigación Científica y Técnica (PB97-0027).

References

1. García de la Vega JM (1995) J Chem Phys 102: 9626
2. Morse MD (1986) Chem Rev 86: 1049
3. Duley WW (1967) Proc Phys Soc 91: 976
4. Freedhoff HS (1967) Proc Phys Soc 92: 505
5. Miller JC, Andrews L (1978) J Chem Phys 69: 3034
6. Miller JC, Andrews L (1980) Appl Spectrosc 16: 1
7. Vreede HJ, Claridge RFC, Phillips LF (1974) Chem Phys Lett 27: 3
8. Kowalski A, Czajkowski M, Breckenridge WH (1985) Chem Phys Lett 119: 368
9. Stevens WJ (1979) Appl Phys Lett 35: 751
10. Su CH, Liao PK, Huang Y, Liou SS, Brebrick RF (1984) J Chem Phys 81: 11
11. Czajkowski M, Bobkowski R, Krause L (1989) Phys Rev A 40: 4338
12. Rodriguez G, Eden JG (1991) J Chem Phys 95: 5539
13. Bender CF, Rescigno TN, Schaefer HF III, Orel AE (1979) J Chem Phys 71: 1122
14. Czuchaj E, Rebentrost F, Stoll H, Preuss H (1994) Chem Phys Lett 225: 233
15. Aguado A, García de la Vega JM, Miguel B (1997) J Chem Soc Faraday Trans 93: 29
16. Huzinaga S (1985) Comput Phys Rep 2: 279
17. Pitzer RM (1977) QCPE Bull 10: 14
18. Clementi E, Roetti C (1974) At Data Nucl Data Tables 14: 177
19. Buenker RJ (1980) Proceedings of a workshop on quantum chemistry and molecular physics, Wollongong, Australia
20. Buenker RJ (1982) Current aspects of quantum chemistry, Elsevier, Amsterdam
21. Buenker RJ, Phillips RA (1985) J Mol Struct (THEOCHEM) 123: 291
22. Fernández Rico J, López R, Aguado A, Ema I, Ramírez G (1999) J Comput Chem 19: 1284
23. García de la Vega JM, Miguel B, Ramírez G (1996) J Phys B 29: 5273
24. Bruna PJ, Peyerimhoff SD, Buenker RJ (1974) Chem Phys Lett 72: 278
25. Langhoff SR, Davidson ER (1974) Int J Quantum Chem 8: 61
26. Moore CE (1952) Atomic energy levels. National Bureau of Standards. (US Government Printing Office, Washington, DC
27. Boys SF, Bernardi F (1970) Mol Phys 19: 553
28. Winans JG (1931) Philos Mag 7: 555
29. Hamada H (1931) Philos Mag 12: 50
30. Carlson KD, Kuschnir KR (1964) J Chem Phys 68: 1566
31. Koga T, Seki Y, Thakkar AJ (1993) Bull Chem Soc Jpn 66: 3135