

Interpair and intrapair electron correlation of low excited states (2A_1) in NaCl_2

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The interpair and intrapair electron pair correlation energies of the low-energy 2A_1 excited state of NaCl_2 have been analyzed and compared with the corresponding energies of the ground 2B_2 states. The total interpair electron correlation energy in the excited state dominates, just as in the ground state. [S1050-2947(97)01903-3]

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INTRODUCTION

Much attention has been paid to electron correlation problems by theoreticians since the early 1960s. Sinanoğlu [1] defined exact electron-pair correlation energies, and did empirical calculations of those pair energies [2]. Nesbet [3] and Davidson and co-workers [4–6] did *ab initio* calculations of some electron pair energies. In 1995, Ju *et al.* [7] published a systematic calculation of the interpair and intrapair electron correlation energies for the ground state 2B_2 of NaCl_2 . They pointed out that since the interpair correlation predominates, the assumption of the Pople *et al.* G_1 [8] and G_2 [9] methods for correcting deficiencies in the electron correlation of molecules is justified only if most of the error is in the smaller interpair correlation. Also, there is no theoretical justification for using $N/2$ rather than $N(N-1)/2$ as the number of pairs in the Pople correction for quadruple excitation [10] or the Ahlrichs average pair correlation energy [11].

All of the Ju *et al.* [7] conclusions are based only on the calculation results for NaCl_2 (C_{2v}) in its ground state, 2B_2 , i.e., $(1-10)a_1^2(1-7)b_2^28b_2^2(1-2)a_2^2(1-3)b_1^2$. How about the electronic excited state? How does the excited electron affect a change in intrapair and interpair correlation? Does the interpair correlation still predominate? In order to answer these questions, the low excited state, $(1-9)a_1^210a_1^1(1-8)b_2^2(1-2)a_2^2(1-3)b_1^2$, of NaCl_2 was taken as an example, doing the calculations at the same level as for the ground state of NaCl_2 , making the comparison between them reasonable. The ground state of NaCl_2 may be described, approximately, as Na^+Cl_2^- with the odd electron in the σ^* orbital of Cl_2 . This excited state is still Na^+Cl_2^- with a $\pi \rightarrow \sigma^*$ excitation of the Cl_2^- . This leaves the odd electron in an orbital of the same symmetry as the $3s$ orbital of Na , but the calculation shows that the orbital remains localized on Cl_2 .

COMPUTATION DETAILS

The electron correlation energy is written as [1]

$$E_c = \langle \psi_{\text{HF}} | H - E_{\text{HF}} | \psi \rangle, \quad (1)$$

where ψ_{HF} is the Hartree-Fock wave function with energy E_{HF} , and ψ is the exact wave function (in intermediate nor-

malization $\langle \psi | \psi_{\text{HF}} \rangle = 1$). The exact wave function is expanded in a series of configurations $\psi_{ij\dots}^{ab\dots}$ with electrons excited from orbitals $ij\dots$ to orbitals $ab\dots$;

$$\psi \equiv \psi_{\text{HF}} + \sum C_j^a \psi_j^a + \sum C_{ij}^{ab} \psi_{ij}^{ab} + \dots \quad (2)$$

Inserting Eq. (2) into Eq. (1) gives

$$E_c = \sum \varepsilon_j + \sum_{i < j} \varepsilon_{ij}, \quad (3)$$

where

$$\varepsilon_i = \sum_a \langle \psi_{\text{HF}} | H | \psi_i^a \rangle C_i^a, \quad (4)$$

$$\varepsilon_{ij} = \sum_{ab} \langle \psi_{\text{HF}} | H | \psi_{ij}^{ab} \rangle C_{ij}^{ab}. \quad (5)$$

In all calculations the $6-31.1+G^*$ split valence polarization basis set was used at the equilibrium geometry reported by Ju and Davidson [12]. The electron correlation calculations were carried out using the MP2-OPT1 method [13,14] for the low excited state 2A_1 . The molecular orbitals used are the ROHF canonical orbitals as described in Ref. [14]. All calculations were performed using the MELD suite of electronic structure codes [15]. The interpair correlations were further summed over all spin combinations and actually represent four electron pairs when both orbitals are doubly occupied.

COMPUTATION RESULTS AND DISCUSSION

A. Intrapair correlations

Table I shows that the correlation energies of the electron pairs, which are in different molecular orbitals, are very different, such as 11.62 mhartree for the $2a_1^2$ pair but only 0.80 millihartree for $5a_1^2$ or $4b_2^2$. Notice that $\varepsilon(5a_1^2) = \varepsilon(4b_2^2)$, $\varepsilon(3a_1^2) = \varepsilon(2b_2^2)$, $\varepsilon(4a_1^2) = \varepsilon(3b_2^2)$, etc., which shows the degeneracy of the electron correlation energies. This phenomenon occurs for the electrons in the delocalized orbitals of inner shells of Cl_2^- (see Table II, which gives the correspondence between molecular orbitals and atomic orbitals.

TABLE I. Pair correlation energies contributions (millihartrees) for the 2A_1 state of NaCl_2 molecule.

$1a_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$	$6a_1$	$7a_1$	$8a_1$	$9a_1$	$10a_1$	$1b_2$	$2b_2$	$3b_2$	$4b_2$	$5b_2$	$6b_2$	$7b_2$	$8b_2$	$1b_1$	$2b_1$	$3b_1$	$1a_2$	$2a_2$	
$1a_1$	5.27																						
$2a_1$	0.00	11.62																					
$3a_1$	1.03	0.00	1.11																				
$4a_1$	0.24	0.00	1.76	0.90																			
$5a_1$	0.24	0.00	1.62	1.22	0.80																		
$6a_1$	0.00	1.74	0.00	0.00	0.00	3.00																	
$7a_1$	0.00	0.59	0.00	0.00	0.00	10.13	8.98																
$8a_1$	0.10	0.00	0.35	0.59	0.50	0.03	0.07	3.80															
$9a_1$	0.02	0.00	0.27	0.37	0.26	0.07	0.17	5.71	6.24														
$10a_1$	0.01	0.00	0.13	0.13	0.17	0.04	0.08	2.34	5.58	0.00													
$1b_2$	10.53	0.00	1.03	0.24	0.24	0.00	0.00	0.10	0.02	0.01	5.27												
$2b_2$	1.03	0.00	2.22	1.76	1.62	0.00	0.00	0.35	0.27	0.13	1.03	1.11											
$3b_2$	0.24	0.00	1.76	1.81	1.21	0.00	0.00	0.58	0.36	0.13	0.24	1.76	0.90										
$4b_2$	0.24	0.00	1.62	1.21	1.60	0.00	0.00	0.50	0.26	0.17	0.24	1.62	1.22	0.80									
$5b_2$	0.00	0.59	0.00	0.00	0.00	10.12	17.77	0.07	0.14	0.09	0.00	0.00	0.00	0.00	8.97								
$6b_2$	0.10	0.00	0.37	0.63	0.54	0.01	0.04	7.79	5.90	2.63	0.10	0.37	0.63	0.54	0.03	4.27							
$7b_2$	0.02	0.00	0.29	0.34	0.33	0.09	0.20	7.24	13.48	6.76	0.02	0.30	0.34	0.33	0.18	8.00	9.87						
$8b_2$	0.02	0.00	0.32	0.38	0.34	0.02	0.05	7.40	13.80	6.86	0.02	0.32	0.39	0.34	0.05	8.04	19.77	10.26					
$1b_1$	0.24	0.00	1.63	1.23	1.12	0.00	0.00	0.51	0.33	0.17	0.24	1.63	1.23	1.11	0.00	0.55	0.37	0.40	0.81				
$2b_1$	0.00	0.59	0.00	0.00	0.00	10.21	17.91	0.06	0.14	0.08	0.00	0.00	0.00	0.00	17.89	0.02	0.16	0.03	0.00	9.08			
$3b_1$	0.02	0.00	0.27	0.36	0.33	0.02	0.05	5.66	10.20	5.53	0.02	0.27	0.36	0.33	0.04	5.94	12.69	12.87	0.26	0.04	6.15		
$1a_2$	0.24	0.00	1.63	1.23	1.11	0.00	0.00	0.51	0.33	0.17	0.24	1.63	1.23	1.12	0.00	0.55	0.37	0.40	1.62	0.00	0.26	0.81	
$2a_2$	0.01	0.00	0.29	0.40	0.36	0.01	0.03	6.05	10.81	5.94	0.02	0.29	0.40	0.36	0.02	6.52	15.59	15.90	0.28	0.02	13.05	0.28	7.18

The x direction is out of plane and the z direction is the C_2 axis). For the electrons in the orbitals of the valence shell, such as $(8-10)a_1$, $(6-8)b_2$, $3b_1$ and $2a_1$, the correlations are much larger and very different, hence no degeneracy occurs. This means that the orbitals of inner shells retain their atomic nature and the orbitals of outer shells mix strongly. The general character of the low excited state 2A_1 is similar to that of the ground state 2B_2 but the total intrapair correlation energy of the 2A_1 state is 5.15 millihartree more than that of the 2B_2 state.

B. Interpair correlations

It is expected, like intrapair correlation, that the variation of interpair correlations is very large for the electron pairs in various orbitals. In Table I, the largest is 19.77 millihartree for $\epsilon(7b_2, 8b_2)$. The interpair results with one electron in a

TABLE II. Main component of the RHF MO's at C_{2v} symmetry of NaCl_2 molecule.

$1a_1$	$1s_{\text{Cl}}$	$2a_1$	$1s_{\text{Na}}$
$3a_1$	$2s_{\text{Cl}}$	$4a_1$	$2p_{x\text{Cl}}$
$5a_1$	$2p_{z\text{Cl}}$	$6a_1$	$2s_{\text{Na}}$
$7a_1$	$2p_{z\text{Na}}$	$8a_1$	$3s_{\text{Cl}}$
$9a_1$	$3p_{z\text{Cl}}$	$10a_1$	$3p_{x\text{Cl}}$
$1b_2$	$1s_{\text{Cl}}$	$2b_2$	$2s_{\text{Cl}}$
$3b_2$	$2p_{x\text{Cl}}$	$4b_2$	$2p_{z\text{Cl}}$
$5b_2$	$2p_{x\text{Na}}$	$6b_2$	$3s_{\text{Cl}}$
$7b_2$	$3p_{z\text{Cl}}$	$8b_2$	$3p_{x\text{Cl}}$
$1b_1$	$2p_{y\text{Cl}}$	$2b_1$	$2p_{y\text{Na}}$
$3b_1$	$3p_{y\text{Cl}}$	$1a_2$	$2p_{y\text{Cl}}$
$2a_2$	$3p_{y\text{Cl}}$		

core orbital localized on Na^+ and the other in a core orbital localized on Cl_2^- (see Table II), such as $2a_1^2ka_1^2$ ($k=1,3,4,5,8,9,10$), $2a_1^2Lb_2^2$ ($L=1,2,3,4,6,8$), $2a_1^2Mb_1^2$ ($M=1,3$), and $2a_1^2Na_2^2$ ($N=1,2$), are approximately zero. So these results support the model $\text{Na}^+ + \text{Cl}_2^-$ for the excited state [12].

There are also many degenerate (or nearly degenerate) sets of the interpair correlations energies. One electron from a degenerate set of intraorbital electron pairs combining with one electron from another degenerate set will produce degenerate interpair correlations. For example, the degenerate configurations $1a_1^2$ and $1b_2^2$ combine with K^2 [$K=(2-9)a_1$, $(2-8)b_2$, $(1-3)b_1$ and $(1-2)a_2$], producing the degenerate interpair correlations. Thus, the interpair correlations ener-

TABLE III. Single excitation energy contributions (millihartrees) for the 2B_2 and 2A_1 states of NaCl_2 molecule.

	2B_2 [7]	2A_1		2B_2	2A_1
$1a_1$	0.00	0.00	$2a_1$	0.00	0.00
$3a_1$	0.01	0.00	$4a_1$	0.02	0.01
$5a_1$	0.00	0.00	$6a_1$	0.00	0.00
$7a_1$	0.00	0.00	$8a_1$	1.67	1.85
$9a_1$	2.14	0.03	$10a_1$	5.97	0.00
$1b_2$	0.00	0.00	$2b_2$	0.01	0.00
$3b_2$	0.02	0.01	$4b_2$	0.00	0.00
$5b_2$	0.00	0.00	$6b_2$	2.53	1.46
$7b_2$	0.12	2.29	$8b_2$	0.00	2.31
$1b_1$	0.00	0.00	$2b_1$	0.00	0.00
$3b_1$	0.09	0.03	$1a_2$	0.00	0.00
$2a_2$	0.10	0.02			
E_{total}	12.68	8.01			

TABLE IV. Intrashell and intershell correlation energy contributions (millihartrees) for the 2B_2 and 2A_1 states of NaCl₂ molecule.

	K_{Na}	L_{Na}	K_{Cl}	L_{Cl}	M
	2B_2 [7]				
K_{Na}	11.62				
L_{Na}	3.50	113.94			
K_{Cl}	0.00	0.00	21.07		
L_{Cl}	0.00	0.00	7.01	48.90	
M	0.01	2.26	0.62	22.20	283.35
One-body	0.00	0.00	0.00	0.06	12.62
	2A_1				
K_{Na}	11.62				
L_{Na}	3.51	114.06			
K_{Cl}	0.00	0.00	21.07		
L_{Cl}	0.00	0.00	7.00	48.77	
M	0.00	2.15	0.61	22.38	295.82
One-body	0.00	0.00	0.00	0.02	7.99

gies in the first column of Table I may be seen as a dual of its eleventh column and row. So Table I consists of some duals and pseudoduals.

The interpair effect (overlap) is strong in some orbital pairs, such as the $2s2p$ and $2p_x2p_y$ interpairs in Na and in Cl, and $3s3p$ and $3p_z3p_y$ in Cl. This leads to a predominance of interpair correlations.

It is interesting to note that the interpair correlation between the symmetry delocalized core orbitals (see Table II) is twice that of the intrapair correlation corresponding to that orbital, such as 10.53 millihartree for $1a_11b_2$, but 5.27 millihartree for $1a_1^2$ or $1b_2^2$. This can be understood by the fact that the total second order correlation in identical nonoverlapping atomic core orbitals a and b , with negligible ε_{ab} , can be given as the sum

$$E_c(a^2b^2) = \varepsilon_{aa} + \varepsilon_{bb} = \varepsilon[(a+b)^2] + \varepsilon[(a-b)^2] + \varepsilon[(a+b), (a-b)], \quad (6)$$

where

$$\varepsilon[(a+b)^2] = \varepsilon[(a-b)^2] = \frac{1}{2}\varepsilon[(a+b), (a-b)] = \frac{1}{2}\varepsilon_{aa} = \frac{1}{2}\varepsilon_{bb}. \quad (7)$$

C. One-body contribution to the correlation energy

Table III shows that most one-body contributions are approximately zero, except those of $8a_1$, $6b_2$, $7b_2$, and $8b_2$. This is different from the ground state 2B_2 and can be understood based on space orbitals. These are the effects of Brillouin-allowed ‘‘single’’ excitations. True single excitations are Brillouin forbidden and make no contribution. The

TABLE V. Total intrapair and interpair correlation energy contributions (millihartrees) for the 2B_2 and 2A_1 states of NaCl₂ molecule.

	Single	Intrapair	Interpair	E_{total}
2B_2 [7]	12.68	102.03	412.46	527.17
	2.4%	19.4%	78.2%	
2A_1	8.01	107.20	419.79	535.00
	1.5%	20.0%	78.5%	

total one-body contributions of the low excitation state 2A_1 is less than that of the ground state 2B_2 and is about 1.5% of the total correlation energy.

D. Intrashell and intershell correlation energy

Table IV shows the total intrashell and intershell correlation energies for low excited state 2A_1 . The intrashell correlation dominates, but the intershell is not negligible. The M intrashell correlation energy is 56.8% of total correlation energy, much larger than those of the other intrashells. The intershell correlations between the Na shell and the Cl shell are mostly zero. This supports the model $\text{Na}^+ + \text{Cl}_2^-$. The M intrashell correlations of the 2A_1 state is -7.84 millihartree more than that of the ground state, 2B_2 . The intershell correlations are almost the same for both states 2B_2 and 2A_1 . So a frozen core calculation of the excitation energy should be valid.

CONCLUSIONS

The main conclusions emerging from the present calculations, which are the answers to the problems posed in the Introduction are the following: (1) There is no universal constant value for the intrapair or interpair electron correlations in both ground state 2B_2 and low excited state 2A_1 of NaCl₂. (2) The interpair correlation still predominates for the low excited state 2A_1 of NaCl₂. It is responsible for 78.5% of the total correlation. Thus, this supports our previous conclusion [7]. Therefore, a fundamental assumption underlying the so-called ‘‘higher level corrections’’ is flawed, based on our calculations of the ground state, 2B_2 , and the low excited state 2A_1 of NaCl₂. (3) The interpair electron correlation energies have to be considered in building models for correcting the post-HF calculations. (see Table V).

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