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# Valence Bond Treatment of Systems Involving Orbital Degeneracy

## II. Application to Benzyl Radical

IDA VANDONI and MASSIMO SIMONETTA
Istituto di Chimica Fisica dell'Università di Milano (Italy)

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A semiempirical valence-bond treatment including polar structures has been developed. Explicit formulas are given for the calculation of energy matrix elements and of charge and spin densities. The method has been applied to benzyl and allyl radicals and to butadiene.

Es wurde ein semiempirisches Valence-Bond-Verfahren einschließlich Polar-Strukturen entwickelt. Explizite Formeln werden für die Berechnung von Energiematrixelementen und für die Ladungs- und Spin-Dichte angegeben. Die Methode wurde auf das Benzyl- und das Allyl-Radikal und auf Butadien angewendet.

On a dévelopé un traitment semi-empirique de la méthode des orbitals de valence avec inclusion des structures polaires. On donne des formules explicitées pour le calcul des éléments matriciels de l'énergie et des densités de charge et de spin. On a appliqué la méthode aux radicaux benzylique et allylique et à la molecule du butadiène.

## Introduction

The semiempirical valence-bond (VB) method has been extensively used in recent years for the calculation of $\pi$-electron charge and spin densities in molecules, radicals and ions [1, 2, 3]. Most of these calculations do not include polar structures, and it has been suggested [4] that such simplification, which exaggerates the amount of electron correlation, can lead to considerable errors in the evaluation of spin densities.

In the present paper the problem of inclusion of polar structures has been considered. The method has been applied to a few simple systems for which results from the *a priori* VB treatment were available [5], and to benzyl radical, which had been the object of extensive experimental and theoretical investigations [4].

## Theoretical Considerations

For a molecular system with $N$ (even or odd) electrons, the wave functions are written in the form

$$\Psi_k = \sum_{r=1}^{R} \sum_{l=1}^{L_r} C_{krl} \varphi_l^r \tag{1}$$

where $r$ labels the electron distribution, $k$ the states and $l$ the structures. $R$ is the number of electron distributions and $L_r$ the number of structures belonging to the

$r$-th distribution. In this work all systems are neutral alternant hydrocarbons (molecules or radicals) with each carbon atom contributing one orbital to the $\pi$-system. Only non polar and singly polar structures with charges on adjacent atoms, which we call orthopolar, are included. The number of electrons and available orbitals are equal and when the geometry of the system is given, the possible distributions of electrons among the orbitals are easily obtained. For each electron distribution the structures can be obtained by application of Rumer rules. Of course if $N$ is odd, a phantom orbit must be included [6]. Doubly occupied and non occupied orbitals don't need to be shown on Rumer diagrams.

$C_{krl}$ are obtained on solving the system of equations

$$\sum_{r=1}^{R} \sum_{i=1}^{L_r} C_{kri}[H_{i,j}^{r,s} - E_k \Delta_{i,j}^{r,s}] = 0 \qquad \begin{matrix} s=1 \ldots R\,, \\ j=1 \ldots L_s\,. \end{matrix} \tag{2}$$

Rules to evaluate the matrix elements in Eq. (2) have been reported [2, 7, 8], both for the case that $M = N$ ($M$ is the number of orbitals appearing in a given structure) and for $M \neq N$. Two different approximations are frequently used when calculating matrix elements: differential overlap can be completely neglected or terms up to second order in overlap may be retained.

Following Schug the second approximation has been used; integrals of the type $\langle a(1)b(2) \ldots |O| a'(1)b(2)\rangle$, where $O$ is $H$ or 1, have been considered of second order if $a$ and $a'$ are next neighbour. To simplify the set up of canonical structures the following prescriptions were adopted. The available orbitals have been numbered in such a way that orbitals centred on adjacent atoms have different parity. The phantom orbit, when necessary, is located in the last position.

All bonds in canonical structures are between an even and an odd orbital. In the fundamental permutation the orbitals are aligned according to their number, with an $\alpha$-spin function coupled with odd orbitals and a $\beta$-function with even orbitals. In ionic structures if $p$ is the empty orbital and $q$ is the doubly occupied orbital, the fundamental permutation is the following one:

$$1\ 2 \ldots p-1\ q\ p+1 \ldots q-1\ q\ q+1 \ldots N$$

(in this example $p < q$). Since the charges are always on adjacent atoms, the parity of $p$ and $q$ are different so the spin assignement to the $p$-th and $q$-th electrons are $\alpha$ and $\beta$ or $\beta$ and $\alpha$ according to the fact that $q$ is even or odd. Then in the superposition diagrams the fundamental permutations always correspond to spin matching. When the matrix elements $H_{i,j}^{r,s}$ and $\Delta_{i,j}^{r,s}$ have been calculated (see next section) the secular determinant and Eqs. (2) have been solved, we obtain the ground state function

$$\Psi_0 = \sum_{r=1}^{R} \sum_{l=1}^{L_r} C_{0,r,l} \mathring{\varphi}_l^r\,. \tag{3}$$

The charge and spin densities at position $r$ are given by the following expressions [9]:

$$Q(r) = P^+(r) + P^-(r) \tag{4}$$

and

$$\varrho(r) = P^+(r) - P^-(r) \tag{4'}$$

where $P^+$ and $P^-$ are the $\alpha$ and $\beta$ spin electron density, respectively, defined as follows:

$$P^{\pm} = N \int |\Psi(\boldsymbol{r}_1, \pm \tfrac{1}{2}; \boldsymbol{r}_2, \omega_2; \ldots \boldsymbol{r}_N, \omega_N)|^2 \, d\tau_2 \ldots d\tau_N \tag{5}$$

where the integration is over spin and space coordinates of $N-1$ electrons.

By substituting $\Psi$ in Eq. (5) from Eq. (3) we get:

$$\begin{aligned} P^{\pm} &= \sum_{r,s} \sum_{i,j} C^*_{0\tau i} C_{0sj} N \int \varphi_i^{r*}(\boldsymbol{r}_1, \pm \tfrac{1}{2}; \ldots \boldsymbol{r}_N, \omega_N) \, \varphi_j^s(\boldsymbol{r}_1, \pm \tfrac{1}{2}; \ldots \boldsymbol{r}_N, \omega_N) d\tau_2 \ldots d\tau_N \\ &= \sum_{r,s} \sum_{i,j} C^*_{0ri} C_{0sj} P^{r,s\pm}_{i,j}(\boldsymbol{r}) \,. \end{aligned} \tag{6}$$

If $a$ and $b$ are two of the available atomic orbitals, we may write

$$P^{r,s\pm}_{i,j}(\boldsymbol{r}) = \sum_{a,b}{}_1^N P^{r,s\pm}_{i,j}(a,b)\, a^*(\boldsymbol{r}) b(\boldsymbol{r}) \tag{7}$$

and hence

$$\begin{aligned} Q(\boldsymbol{r}) &= \sum_{a,b} a^*(\boldsymbol{r}) b(\boldsymbol{r}) \sum_{r,s} \sum_{i,j} C^*_{0ri} C_{0sj} \{P^{r,s+}_{i,j}(a,b) + P^{r,s-}_{i,j}(a,b)\} \\ &= \sum_{a,b} a^*(\boldsymbol{r}) b(\boldsymbol{r}) Q(a,b) \,, \end{aligned} \tag{8}$$

$$\begin{aligned} \varrho(\boldsymbol{r}) &= \sum_{a,b} a^*(\boldsymbol{r}) b(\boldsymbol{r}) \sum_{r,s} \sum_{i,j} C^*_{0ri} C_{0sj} \{P^{r,s+}_{i,j}(a,b) - P^{r,s-}_{i,j}(a,b)\} \\ &= \sum_{a,b} a^*(\boldsymbol{r}) b(\boldsymbol{r}) \varrho(a,b) \,, \end{aligned} \tag{8'}$$

where the sums are over all occupied orbitals, and all structures.

## Calculations

The matrix elements $H^{r,s}_{i,j}$ appearing in Eq. (2) are built by a combination of many integrals; these can be divided in four classes:

a) Coulomb integrals:

$$Q(r) = \langle a(1) b(2) \ldots | \mathscr{H} | a(1) b(2) \ldots \rangle \,. \tag{9}$$

b) Exchange integrals:

$$\varepsilon(r) = \langle a(1) b(2) \ldots | \mathscr{H} | b(1) a(2) \ldots \rangle \,. \tag{10}$$

c) First order electron transfer integrals,

$$\tau_1(r,s) = \langle a(1) b(2) \ldots | \mathscr{H} | a'(1) b(2) \ldots \rangle \,. \tag{11}$$

d) Second order electron transfer integrals:

$$\tau_{1,1}(r,s) = \langle a(1) b(2) \ldots | \mathscr{H} | a'(1) b'(2) \ldots \rangle \tag{12}$$

$$\tau_2(r,s) = \langle a(1) b(2) \ldots | \mathscr{H} | a''(1) b(2) \ldots \rangle \,. \tag{12'}$$

In the preceeding formulas $a$ and $a'$, $b$ and $b'$ are centered on adjacent atoms, $a$ and $a''$ on next neighbour atoms.

To simplify our formulas for matrix elements all integrals in classes b, c, d, have been assumed to be independent from the electron distributions $u$ and $v$. The various integrals have been actually calculated for all cases and the numerical values are so close that the above assumption and the use of an average value for each kind of integrals is amply justified. Besides, all the integrals of the type $\varepsilon$ and $\tau_{11}$ have similar values and their averages are also very close so that one general average value has been used for both. In particular it can be shown [10] that second order transfer integrals $\langle a(1)a(2)\ldots|\mathscr{H}|a'(1)a'(2)\ldots\rangle$ are equal to exchange integrals $\langle a(1)a'(2)\ldots|\mathscr{H}|a'(1)a(2)\ldots\rangle$. For coulomb integrals the value corresponding to the non polar distribution is significantly different from values for polar distributions, which are all very close to each other so that two values have been used: $Q$ for the non polar distribution and $Q'$, the average value for polar distributions.

To summarize, the following integrals appear in matrix elements for the energy operator:

$$Q, Q', \varepsilon, \tau_1 \text{ and } \tau_2 .$$

In the same approximation, two average values for the overlap integrals are used:

$$S = \langle a|a'\rangle \quad \text{and} \quad S' = \langle a|a''\rangle . \tag{13}$$

To calculate the integrals the geometry of the system is needed. Our assumed geometries are given in Fig. 1, together with the numbering of the atoms.

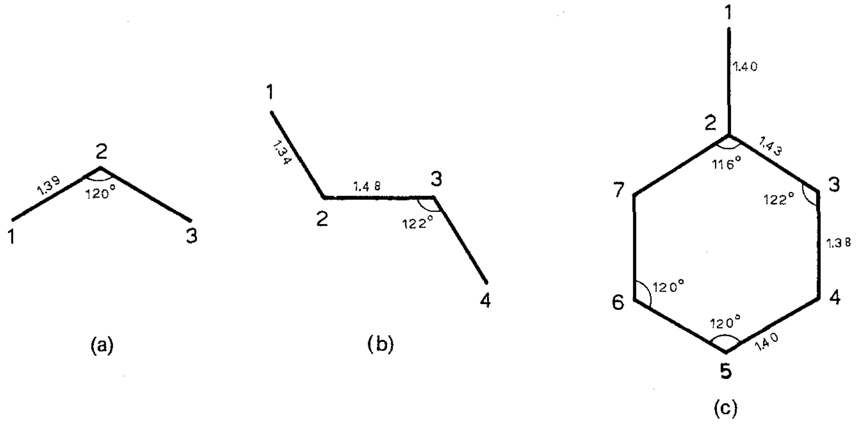

Fig. 1. Numbering of atoms and geometries of (a) allyl radical, (b) butadiene, (c) benzyl radical. Bond length in Å, bond angles in degrees

The formulas for matrix elements

$$H^{r,s}_{i,j} = \langle \varphi^r_i|\mathscr{H}|\varphi^1_j\rangle \tag{14}$$

$$\Delta^{r,s}_{i,j} = \langle \varphi^r_i|\varphi^s_j\rangle \tag{14'}$$

and $P^{r,s}_{ij}(a,a)$ can now be written. Three different situations occur:

a) $r=s$. Then

$$H_{i,j}^{r,r}=\frac{1}{2^{n-i}}\left[Q^*+\sum_{u,v}{}'(1+\delta_{uq}+\delta_{vq})\,f(u,v)\varepsilon\right], \tag{15}$$

$$\Delta_{i,j}^{r,r}=\frac{1}{2^{n-i}}\left[1+\sum_{z,v}{}'(1+\delta_{uq}+\delta_{vq})\,f(u,v)S^2\right], \tag{15'}$$

$$\begin{aligned}P_{i,j}^{r,r\pm}(a,a)=(1-\delta_{ap})\,(1+\delta_{aq})\frac{1}{2^{n-i}}\Bigg\{&\frac{1}{2}\pm\Lambda_{00}^{a}\\&+S^2\Bigg[\sum_{\substack{u,v\neq p\\ \neq a}}f(u,v)\,(1+\delta_{uq}+\delta_{vq})\left(\frac{1}{2}\pm\Lambda_{uv}^{a}\right)\\&+\delta_{aq}\sum_{u}{}''f(u,a)\left(\frac{1}{2}\pm\Lambda_{au}^{p}\right)\Bigg]\Bigg\}.\end{aligned} \tag{15''}$$

$Q^*$ is equal to $Q(Q')$ if $r$ is a covalent (ionic) distribution. $\sum'$ is over all pairs of orbitals centered on adjacent atoms; $\sum''$ is over all orbitals adjacents to $a$; $\delta$ is the Kronecker symbol; $n$ is equal to $N/2$ if $N$ is even or $\frac{N+1}{2}$ if $N$ is odd; $i$ is the number of islands in the superposition diagrams for the two structures in the fundamental permutation; $f(u,v)$ is equal to 1 if orbitals $u$ and $v$ belong to the same island, and equal to $-1/2$ if they belong to different islands. $\Lambda_{yz}^{x}$ is equal to 0 if the orbital in position $x$ and the phantom orbital $w$ are on different islands, in the superposition diagram, is equal to 1/2 if $x$ and $w$ are in the same island an odd number of bonds apart, is equal to $-1/2$ if $x$ and $w$ are on the same island an even number of bonds apart. When $yz$ is equal to 00 the fundamental permutation of both structures must be used in the superposition diagram, otherwise the fundamental permutation of structure $i$ must be superimposed to the permutation of structure $j$ obtained from the fundamental by exchange of orbital $y$ and $z$.

b) $r$ is the covalent distribution and $s$ one of the polar distributions:

$$H_{i,j}^{r,s}=\frac{\sqrt{2}}{2^{n-i}}\tau, \qquad \Delta_{i,j}^{r,s}=\frac{\sqrt{2}}{2^{n-i}}S, \tag{16}$$

$$P_{i,j}^{r,s\pm}(a,a)=(1-\delta_{ap})\left(\frac{1}{2}\pm\Lambda_{00}^{a}\right)\frac{\sqrt{2}}{2^{n-i}}S. \tag{16'}$$

c) $r$ and $s$ are two different polar distributions:

$$H_{i,j}^{r,s}=\frac{1}{2^{n-i}}\left[(2-2\delta_{pp'}-\delta_{qp'}-\delta_{pq'})\varepsilon+2(\delta_{pp'}-\delta_{qq'})\tau_q\right], \tag{17}$$

$$\Delta_{i,j}^{r,s}=\frac{1}{2^{n-i}}\left[(2-2\delta_{pp'}-\delta_{qp'}-\delta_{pq'})S^2+2(\delta_{pp'}-\delta_{qq'})S\right], \tag{17'}$$

$$P_{i,j}^{r,s}(a,a)=(1-\delta_{ap})\left(\frac{1}{2}\pm\Lambda_{00}^{a}\right)\frac{2S'}{2^{n-i}} \quad \text{if} \quad p=p', \tag{17''}$$

$$\begin{aligned} P_{i,j}^{r,s\pm}(a,a) = (1-\delta_{ap}-\delta_{ap'})\frac{2}{2^{n-i}}\Bigg\{\left(\frac{1}{2}\pm\Lambda_{00}^{a}\right)S^2 \\ -[1+\delta_{aq}\pm 2\Lambda_{00}^{a}(1-\delta_{aq})]\frac{S'}{2}\Bigg\}, \quad \text{if} \quad q=q' \end{aligned} \qquad (17''')$$

$$\begin{aligned} P_{i,j}^{r,s\pm}(a,a) = (1-\delta_{ap}-\delta_{ap'})\frac{S^2}{2^{n-i}}\left(\frac{1}{2}\pm\Lambda_{00}^{a}\right)\cdot(2-\delta_{qp'}\delta_{pq'}) \\ \text{if} \quad p\neq p' \quad \text{and} \quad q\neq q'. \end{aligned} \qquad (17'''')$$

Primed and unprimed $p$'s and $q$'s refer to the two structures.

## Results and Discussion

### *A. Benzyl Radical*

The spectrum of this compound has been analyzed by Carrington and Smith [4] who obtained the following absolute values for the hfs constants: $a_1=16.35$, $a_3=5.14$, $a_4=1.75$, $a_5=6.14$. Theoretical values of these quantities can be obtained from the corresponding spin densities $\varrho_i$ through the McConnell's relationship

$$a_i = Q\varrho_i \qquad (18)$$

where $Q$ is given by

$$Q=\frac{2a_1+2a_3-2a_4+a_5}{2\varrho_1+2\varrho_3+2\varrho_4+\varrho_5}. \qquad (19)$$

Theoretical values of $a_i$ had been previously obtained using the VB method with inclusion of 5 or 14 covalent structures. The agreement with experiment is worse when 14 structures are used and this fact was considered as due to the exaggerated electron correlation.

We included 70 ortho-polar structures besides the 14 covalent structures. The values of integrals obtained from the averaging of the theoretical values (see Appendix I) are (in a.u.):

$Q=-6.85$, $Q'=-6.56$, $\varepsilon=-0.48$, $\tau_1=-1.82$, $\tau_2=-0.26$, $S=0.2547$, $S'=0.0364$.

The predicted hfs constants are shown in Table 1, together with previously calculated and experimental constants.

Table 1. *Predicted* hfs *constants (in Gauss): $Q=24.28$*

| | $a_1$ | $a_3$ | $a_4$ | $a_5$ |
|---|---|---|---|---|
| 5 covalent structures | 15.58 | 7.50 | 4.03 | 7.50 |
| 14 covalent structures | 15.04 | 9.41 | 5.92 | 8.55 |
| 14 covalent + 70 ortho-polar structures | 14.78 | 8.94 | 5.03 | 8.33 |
| Experimental | 16.35 | 5.14 | 1.75 | 6.14 |

The results are slightly improved with respect to the ones given by the full covalent treatment, but are still worse than the more simplified calculations. It seems that electron correlation has not been reduced as much as it should and perhaps meta and para polar structures are needed.

It might be thought that the choice of integrals has not been a happy one. However it has been already pointed out [7] that spin densities calculated by the VB method are not very sensitive to the values assumed for the integrals. Considering the integrals as parameters, calculations performed with different sets of extimated values for such parameters, within reasonable ranges, lead to results not significantly affected.

### *B. Allyl Radical and Butadiene*

For sake of comparison, two simple systems, allyl radical and butadiene were treated in the same approximation.

The results for allyl radical can be compared (see Table 2) with values previously obtained by the *a priori* VB method [5], and with experimental values, when available.

Table 2. *$\pi$-electron energy and spin densities for allyl radical*

| | This work 6 structures | This work 2 covalent structures | Ref. 5 | Exp. [11] |
|---|---|---|---|---|
| $\varrho_1$ | 0.630 | 0.677 | 0.622 | 0.589 |
| $\varrho_2$ | $-0.228$ | $-0.312$ | $-0.206$ | $-0.155$ |
| $\varrho_1/\varrho_2$ | $-2.76$ | $-2.17$ | $-3.02$ | $-3.80$<br>$(a_1/a_2 = -3.54)$ |
| $E$ (a.u.) | $-1.76$ | $-1.70$ | $-1.767$ | |

It seems that while present treatment gives a result very close to the one obtained by the *a priori* method for the energy, spin densities are significantly worse. However for allyl radical the benefit inclusion of polar structures is significant.

For butadiene a $\pi$-electron energy of $-2.81$ a.u. was obtained, to be compared with $E = -2.85$ *(cis)* and $-2.82$ *(trans)* from the *a priori* method.

## Appendix I

As an example we give the values obtained for the different first order electron transfer integrals, from which it may be seen that the difference between the different values and the average is always less than 5%.

$$\langle abcdefg|\mathscr{H}|aacdefg\rangle = -1.8357 \text{ (a.u.)}$$

$$\langle abcdefg|\mathscr{H}|bbcdefg\rangle = -1.8476$$

$$\langle abcdefg|\mathscr{H}|abbdefg\rangle = -1.7547$$

$$\langle abcdefg|\mathscr{H}|accdefg\rangle = -1.7494$$

$$\langle abcdefg|\mathscr{H}|abccefg\rangle = -1,8707$$

$$\langle abcdefg|\mathscr{H}|abddefg\rangle = -1.8713$$

$$\langle abcdefg|\mathscr{H}|abcddfg\rangle = -1.8417$$

$$\langle abcdefg|\mathscr{H}|abceefg\rangle = -1.8415$$

## Appendix II

The structures, the symmetry structures and the ground state wave function (corresponding to $E = -7.04454$ a.u.) for the benzyl radical are shown in the following Tables A1, A2, A3.

Table A1. *Structures*

| $r$ | $i$ | $\varphi_i^r$ | | | | $r$ | $i$ | $\varphi_i^r$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1–2 | 3–4 | 5–6 | 7–8 | 7 | 4 | 3–3 | 1–8 | 2–7 | 5–6 |
| 1 | 2 | 1–4 | 2–3 | 5–6 | 7–8 | 7 | 5 | 3–3 | 1–6 | 2–5 | 7–8 |
| 1 | 3 | 1–6 | 2–3 | 4–5 | 7–8 | 8 | 1 | 5–5 | 1–2 | 3–6 | 7–8 |
| 1 | 4 | 1–8 | 2–3 | 4–5 | 6–7 | 8 | 2 | 5–5 | 1–8 | 2–3 | 6–7 |
| 1 | 5 | 1–2 | 3–8 | 4–5 | 6–7 | 8 | 3 | 5–5 | 1–2 | 3–8 | 6–7 |
| 1 | 6 | 1–2 | 3–4 | 5–8 | 6–7 | 8 | 4 | 5–5 | 1–8 | 2–7 | 3–6 |
| 1 | 7 | 1–2 | 3–8 | 4–7 | 5–6 | 8 | 5 | 5–5 | 1–6 | 2–3 | 7–8 |
| 1 | 8 | 1–2 | 3–6 | 4–5 | 7–8 | 9 | 1 | 4–4 | 1–2 | 3–6 | 7–8 |
| 1 | 9 | 1–4 | 2–3 | 5–8 | 7–6 | 9 | 2 | 4–4 | 1–8 | 2–3 | 6–7 |
| 1 | 10 | 1–6 | 2–5 | 3–4 | 7–8 | 9 | 3 | 4–4 | 1–2 | 3–8 | 6–7 |
| 1 | 11 | 1–8 | 2–7 | 3–4 | 5–6 | 9 | 4 | 4–4 | 1–8 | 2–7 | 3–6 |
| 1 | 12 | 1–8 | 2–3 | 4–7 | 5–6 | 9 | 5 | 4–4 | 1–6 | 2–3 | 7–8 |
| 1 | 13 | 1–8 | 2–7 | 3–6 | 4–5 | 10 | 1 | 7–7 | 1–6 | 4–5 | 3–8 |
| 1 | 14 | 1–8 | 2–5 | 3–4 | 6–7 | 10 | 2 | 7–7 | 1–8 | 6–5 | 3–4 |
| 2 | 1 | 2–2 | 3–4 | 5–6 | 7–8 | 10 | 3 | 7–7 | 1–6 | 5–8 | 3–4 |
| 2 | 2 | 2–2 | 3–8 | 4–5 | 7–6 | 10 | 4 | 7–7 | 1–8 | 6–3 | 4–5 |
| 2 | 3 | 2–2 | 3–4 | 5–8 | 7–6 | 10 | 5 | 7–7 | 1–4 | 3–8 | 5–6 |
| 2 | 4 | 2–2 | 3–8 | 4–7 | 5–6 | 11 | 1 | 2–2 | 1–6 | 4–5 | 3–8 |
| 2 | 5 | 2–2 | 3–6 | 4–5 | 7–8 | 11 | 2 | 2–2 | 1–8 | 5–6 | 3–4 |
| 3 | 1 | 1–1 | 3–4 | 5–6 | 7–8 | 11 | 3 | 2–2 | 1–6 | 5–8 | 3–4 |
| 3 | 2 | 1–1 | 3–8 | 4–5 | 7–6 | 11 | 4 | 2–2 | 1–8 | 3–6 | 4–5 |
| 3 | 3 | 1–1 | 3–4 | 5–8 | 7–6 | 11 | 5 | 2–2 | 1–4 | 3–8 | 5–6 |
| 3 | 4 | 1–1 | 3–8 | 4–7 | 5–6 | 12 | 1 | 6–6 | 1–2 | 4–5 | 3–8 |
| 3 | 5 | 1–1 | 3–6 | 4–5 | 7–8 | 12 | 2 | 6–6 | 1–8 | 3–4 | 2–5 |
| 4 | 1 | 3–3 | 1–4 | 5–6 | 7–8 | 12 | 3 | 6–6 | 1–2 | 5–8 | 3–4 |
| 4 | 2 | 3–3 | 1–8 | 4–5 | 6–7 | 12 | 4 | 6–6 | 1–8 | 2–3 | 4–5 |
| 4 | 3 | 3–3 | 1–4 | 5–8 | 6–7 | 12 | 5 | 6–6 | 1–4 | 2–5 | 3–8 |
| 4 | 4 | 3–3 | 1–8 | 4–7 | 5–6 | 13 | 1 | 7–7 | 1–2 | 4–5 | 3–8 |
| 4 | 5 | 3–3 | 1–6 | 7–8 | 4–5 | 13 | 2 | 7–7 | 1–8 | 4–3 | 2–5 |
| 5 | 1 | 2–2 | 1–4 | 5–6 | 7–8 | 13 | 3 | 7–7 | 1–2 | 5–8 | 3–4 |
| 5 | 2 | 2–2 | 1–8 | 4–5 | 6–7 | 13 | 4 | 7–7 | 1–8 | 2–3 | 4–5 |
| 5 | 3 | 2–2 | 1–4 | 5–8 | 6–7 | 13 | 5 | 7–7 | 1–4 | 2–5 | 3–8 |
| 5 | 4 | 2–2 | 1–8 | 4–7 | 5–6 | 14 | 1 | 5–5 | 1–2 | 4–7 | 3–8 |
| 5 | 5 | 2–2 | 1–6 | 7–8 | 4–5 | 14 | 2 | 5–5 | 1–8 | 2–7 | 3–4 |
| 6 | 1 | 4–4 | 1–2 | 5–6 | 7–8 | 14 | 3 | 5–5 | 1–2 | 7–8 | 3–4 |
| 6 | 2 | 4–4 | 1–8 | 6–7 | 5–2 | 14 | 4 | 5–5 | 1–8 | 2–3 | 4–7 |
| 6 | 3 | 4–4 | 1–2 | 5–8 | 6–7 | 14 | 5 | 5–5 | 1–4 | 2–7 | 3–8 |
| 6 | 4 | 4–4 | 1–8 | 2–7 | 5–6 | 15 | 1 | 6–6 | 1–2 | 4–7 | 3–8 |
| 6 | 5 | 4–4 | 1–6 | 2–5 | 7–8 | 15 | 2 | 6–6 | 1–8 | 2–7 | 3–4 |
| 7 | 1 | 3–3 | 1–2 | 5–6 | 7–8 | 15 | 3 | 6–6 | 1–2 | 7–8 | 3–4 |
| 7 | 2 | 3–3 | 1–8 | 6–7 | 5–2 | 15 | 4 | 6–6 | 1–8 | 2–3 | 4–7 |
| 7 | 3 | 3–3 | 1–2 | 5–8 | 6–7 | 15 | 5 | 6–6 | 1–4 | 2–7 | 3–8 |

Table A2. *Symmetry structures*

$\Psi_1 = \Phi_1^1 + \Phi_5^1$
$\Psi_2 = \Phi_4^1 + \Phi_1^{11}$
$\Psi_3 = \Phi_1^{12} + \Phi_1^{13}$
$\Psi_4 = \Phi_7^1 + \Phi_8^1$
$\Psi_5 = \Phi_6^1$
$\Psi_6 = \Phi_{14}^1$
$\Psi_7 = \Phi_9^1 - \Phi_1^1 + \Phi_{10}^1 + \Phi_{11}^1$
$\Psi_8 = \Phi_3^1 - \Phi_1^1 + \Phi_2^1 + \Phi_7^1 + \Phi_{11}^1 - \Phi_{12}^1$
$\Psi_9 = \Phi_1^2 + \Phi_2^2$
$\Psi_{10} = \Phi_3^2$
$\Psi_{11} = \Phi_4^2 + \Phi_5^2$
$\Psi_{12} = \Phi_1^3 + \Phi_2^3$
$\Psi_{13} = \Phi_3^3$
$\Psi_{14} = \Phi_4^3 + \Phi_5^3$
$\Psi_{15} = \Phi_1^4 + \Phi_1^{10}$
$\Psi_{16} = \Phi_2^4 + \Phi_2^{10}$
$\Psi_{17} = \Phi_3^4 + \Phi_3^{10}$
$\Psi_{18} = \Phi_4^4 + \Phi_4^{10}$
$\Psi_{19} = \Phi_5^4 + \Phi_5^{10}$
$\Psi_{20} = \Phi_1^5 + \Phi_1^{11}$
$\Psi_{21} = \Phi_2^5 + \Phi_2^{11}$
$\Psi_{22} = \Phi_3^5 + \Phi_3^{11}$
$\Psi_{23} = \Phi_4^5 + \Phi_4^{11}$
$\Psi_{24} = \Phi_5^5 + \Phi_5^{11}$
$\Psi_{25} = \Psi_1^6 + \Psi_1^{12}$
$\Psi_{26} = \Psi_2^6 + \Psi_2^{12}$
$\Psi_{27} = \Psi_3^6 + \Psi_3^{12}$
$\Psi_{28} = \Psi_4^6 + \Psi_4^{12}$
$\Psi_{29} = \Psi_5^6 + \Psi_5^{12}$
$\Psi_{30} = \Psi_1^7 + \Psi_1^{13}$
$\Psi_{31} = \Psi_2^7 + \Psi_2^{13}$
$\Psi_{32} = \Psi_3^7 + \Psi_3^{13}$
$\Psi_{33} = \Psi_4^7 + \Psi_4^{13}$
$\Psi_{34} = \Psi_5^7 + \Psi_5^{13}$
$\Psi_{35} = \Psi_1^8 + \Psi_1^{14}$
$\Psi_{36} = \Psi_2^8 + \Psi_2^{14}$
$\Psi_{37} = \Psi_3^8 + \Psi_3^{14}$
$\Psi_{38} = \Psi_4^8 + \Psi_4^{14}$
$\Psi_{39} = \Psi_5^8 + \Psi_5^{14}$
$\Psi_{40} = \Psi_1^9 + \Psi_1^{15}$
$\Psi_{41} = \Psi_2^9 + \Psi_2^{15}$
$\Psi_{42} = \Psi_3^9 + \Psi_3^{15}$
$\Psi_{43} = \Psi_4^9 + \Psi_4^{15}$
$\Psi_{44} = \Psi_5^9 + \Psi_5^{15}$

Table A3. *Ground state wave function*

$$\begin{aligned}\Psi = {} & 0.10242\,\Psi_1 + 0.06896\,\Psi_2 + 0.05643\,\Psi_3 + 0.00316\,\Psi_4 + 0.09927\,\Psi_5 + 0.01162\,\Psi_6 \\ & + 0.02190\,\Psi_7 + 0.03316\,\Psi_8 + 0.04655\,\Psi_9 + 0.03976\,\Psi_{10} + 0.01460\,\Psi_{11} + 0.04953\,\Psi_{12} \\ & + 0.04281\,\Psi_{13} + 0.01516\,\Psi_{14} + 0.01810\,\Psi_{15} + 0.05571\,\Psi_{16} + 0.02079\,\Psi_{17} + 0.03125\,\Psi_{18} \\ & + 0.01288\,\Psi_{19} + 0.01758\,\Psi_{20} + 0.05413\,\Psi_{21} + 0.02009\,\Psi_{22} + 0.03055\,\Psi_{23} + 0.01307\,\Psi_{24} \\ & + 0.03039\,\Psi_{25} + 0.01244\,\Psi_{26} + 0.05678\,\Psi_{27} + 0.05724\,\Psi_{28} + 0.01226\,\Psi_{29} + 0.03057\,\Psi_{30} \\ & + 0.01277\,\Psi_{37} + 0.05604\,\Psi_{32} + 0.05710\,\Psi_{33} + 0.01212\,\Psi_{34} + 0.00654\,\Psi_{35} + 0.03492\,\Psi_{36} \\ & + 0.05932\,\Psi_{37} + 0.03794\,\Psi_{38} + 0.02047\,\Psi_{39} + 0.00636\,\Psi_{40} + 0.03484\,\Psi_{41} + 0.05985\,\Psi_{42} \\ & + 0.03798\,\Psi_{43} + 0.02034\,\Psi_{44}\end{aligned}$$

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Prof. Dr. M. Simonetta
Istituto di Chimica Fisica dell'Università di Milano
Via C. Saldini 50, Milano, Italy