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Atomic Valence States in Molecular Orbital Theory

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Atomic valence states in simple valence bond and molecular orbital theories of electronic structure have been compared. A basic difference emerges which can be characterised by the presence of one-centre Coulomb terms in the molecular orbital valence state energy. The recognition of this difference is important when performing generalised Hückel calculations: the Coulomb integrals are now given by charge dependent orbital electronegativities, and not the negative of the appropriate ionisation potentials of the kind available in the existing tabulations by Hinze and Jaffé and other authors. The analysis is given in detail for the special case of tetrahedrally coordinated boron and nitrogen, as found in cubic boron nitride.

Es werden atomare Valenzzustände in einfachen Valenzbindungen und MO Theorien der Elektronenstruktur verglichen. Ein wesentlicher Unterschied ergibt sich durch die Anwesenheit von Einzentren-Coulomb-Termen in den MO-Valenzzustandsenergien. Das Erkennen dieser Unterschiede spielt eine entscheidende Rolle bei der Durchführung von Berechnungen nach der allgemeinen Hückel-Theorie: die Coulomb-Integrale sind nun durch Z-abhängige Orbitalelektronennegativitäten und nicht durch geeignete Ionisationspotentiale, wie sie in den Tabellen von Hinze und Jaffé und anderen Autoren verfügbar sind, gegeben. An Hand des tetraedisch gebundenen Bors und Stickstoffs, wie sie in kubischen Bornitriden vorkommen, wird eine genaue Analyse der Methode an einem speziellen Beispiel durchgeführt.

Comparaison des états de valence atomiques dans les méthodes de la mésomérie et des orbitales moléculaires. Il apparait une différence fondamentale, que l'on peut caractériser par la présence de termes coulombiens monocentriques dans l'énergie de l'état de valence en orbitales moléculaires. Il importe d'être conscient de cette différence lorsqu'on effectue des calculs Hückel-étendu: les intégrales coulombiennes sont alors données par des électronégativités orbitales dépendant de la charge et non par l'opposé des potentiels d'ionisation du type de ceux que l'on obtient dans les tables de Hinze et Jaffé ou d'autres auteurs. On donne une analyse détaillée pour le cas particulier de l'azote et du bore à coordination tétraédrique, tel qu'il apparait dans le nitrure de bore cubique.

Introduction

The motivation for introducing the valence state concept comes from the extreme difficulty in calculating molecular binding energies from first principles. Quite frequently the molecular binding energy represents only about 1% of the total molecular energy; that is, it may be of the same order of, or less than, the correlation energy error. For this reason, atomic spectral data are frequently incorporated into energy calculations to account for the large intra-atomic contribution to the correlation energy.

One of the first attempts to define a valence state was made by Heitler and Rumer [1]. They regarded the valence state of an atom forming n bonds as the appropriate atomic state of spin multiplicity $n+1$. This valence state does not readily display the directional characteristics normally associated with an atom involved in the formation of n bonds: but some directional character does appear after a proper consideration of second order interchanges, as recently discussed by Heitler [2], and also by Hansen [3]. The lack of directional characteristics is thus partially accounted for; but the Heitler-Rumer valence states is rather a restricted one, as the use of a single valence bond structure is unlikely to yield a good representation of the molecular electronic wave function.

An improved molecular wave function is obtained by using a set of directional orbitals as basis functions, which may be obtained from the set of valence shell atomic functions by a suitable unitary transformation. The perfect pairing approximation is then invoked to yield a single valence bond structure which has bond equivalence built into it – a feature which is missing from the simpler Heitler-Rumer approach, but recently amended by Craig and Thirunamachandran [4]. For example, the ground state of methane is represented by the single structure

$$\Phi = \mathscr{A}\, te_1 h_1\, te_2 h_2\, te_3 h_3\, te_4 h_4$$

where te_i and h_i $(i = 1, 2, 3, 4)$ are carbon tetrahedral hybrids and hydrogen 1s atomic orbitals respectively. After performing the required non-adiabatic dissociation, the valence state energy of carbon is found to consist of contributions from atomic term energies arising from the valence shell configurations s^2p^2, sp^3 and p^4 [5], and not just the sp^3, ${}^5S$ energy as required by Heitler and Rumer:

$$\begin{aligned} E_{vs}(\mathrm{C}) = {} & 0.312\, E(sp^3, {}^5S) + 0.141\, E(p^4, {}^3P) + 0.282\, E(sp^3, {}^3D) \\ & + 0.141\, E(s^2p^2, {}^3P) + 0.047\, E(p^4, {}^1D) \\ & + 0.031\, E(sp^3, {}^1D) + 0.047\, E(s^2p^2, {}^1D) \\ & - 0.093 \langle p^4, {}^1D | H | s^2p^2, {}^1D \rangle - 0.282 \langle p^4, {}^3P | H | s^2p^2, {}^3P \rangle . \end{aligned} \tag{1}$$

The appearance of off-diagonal terms in Eq. (1) arises from the configuration interaction within the pairs of ${}^1D$ and ${}^3P$ states, on account of the single configurational representation of these terms. The valence state energy given in Eq. (1) is also reproduced by the well-known van Vleck formula [6]:

$$E_{vs}(\mathrm{C}) = 4\langle te_1 | -\tfrac{1}{2}\, \nabla^2 + V_{\mathrm{core}} | te_1 \rangle + \sum_{i<j} \{ (te_i te_i | te_j te_j) - \tfrac{1}{2} (te_i te_j | te_i te_j) \} \tag{2}$$

where $(te_i te_j | te_k te_l) = \iint te_i(1) te_j(1) \frac{1}{r_{12}}\, te_k(2)\, te_l(2)\, d\tau_1\, d\tau_2$. The equivalence of Eq. (1) and (2) is most readily seen by rewriting both equations in terms of the more usual Slater-Condon parameters.

The non-stationary character of the valence state is clearly shown in Eq. (1), since L and S are no longer good quantum numbers. However, Eq. (1) still implies a restricted form of valence state: a slightly more general form can be obtained by considering all other covalent structures involving single or double occupancy of the carbon hybrid atomic orbitals. The analysis has again been given by Voge [5], and the valence state energy now has the form:

$$\begin{aligned} E_{vs}(\mathrm{C}) = {} & 0.212\, E(sp^3, {}^5S) + 0.036\, E(p^4, {}^3P) + 0.278\, E(sp^3, {}^3D) \\ & + 0.290\, E(s^2p^2, {}^3P) + 0.017\, E(p^4, {}^1D) \\ & + 0.021\, E(sp^3, {}^1D) + 0.146\, E(s^2p^2, {}^1D) \\ & - 0.101 \langle p^4, {}^1D | H | s^2p^2, {}^1D \rangle - 0.204 \langle p^4, {}^3P | H | s^2p^2, {}^3P \rangle . \end{aligned} \tag{3}$$

The magnitude of the factors weighting the term energies, in Eq. (3), now depend upon the values for certain molecular integrals, and are not determined by symmetry. Permutational symmetry requirements only dictate that the same atomic terms appear in Eqs. (1) and (3), but now place no restrictions on the magnitudes of the respective weighting factors.

The extension of the theory to include ionic structures is an involved procedure, and the appropriate calculation has not yet been made. So instead of proceeding further within a valence bond framework, it is convenient to discuss the role of the valence state in simple molecular orbital theory.

Valence States in Molecular Orbital Theory

A large amount of data have been collected in the literature pertaining to the restricted form of valence state associated with the perfect pairing model. But nearly all semi-empirical electronic structure calculations are performed using some form of molecular orbital theory: it therefore seems desirable to examine the concept of a restricted form of atomic valence state in a single configuration molecular orbital theory. This is important as an increasing number of semi-empirical molecular orbital calculations on large molecules, notably of the extended Hückel variety [7, 8], usually incorporate valence state data which have been calculated from Van Vleck's perfect pairing formula, in the manner originally given by Mulliken [9]: a procedure which obviously requires careful justification.

The simplest valence bond and molecular orbital theories of chemical bonding are based on fundamentally different assumptions. The valence bond method over-correlates the electronic motion since electrons with opposed spins, involved in the formation of electron-pair bonds, are on average associated with different atoms. The molecular orbital theory, on the other hand, is based on the idea of delocalised one-electron functions (molecular orbitals), extending over the entire molecular framework. For a closed shell molecule, where each occupied molecular orbital accommodates two electrons with opposed spins, the electronic motion tends to be under-correlated. The degree of electronic correlation in the two simple theories is best examined by comparing the diagonal elements of the appropriate two-electron density matrices. For the simple case of H_2, these density matrix elements are given by

$$\begin{aligned}\Gamma(1,2;1,2)_{\mathrm{mo}} = {} & \tfrac{1}{4}\{\varphi_a^2(1) + 2\varphi_a(1)\,\varphi_b(1) + \varphi_b^2(1)\} \\ & \times\{\varphi_a^2(2) + 2\varphi_a(2)\,\varphi_b(2) + \varphi_b^2(2)\} \\ & \times\tfrac{1}{2}\{\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)\}^2\,,\end{aligned}$$

$$\begin{aligned}\Gamma(1,2;1,2)_{\mathrm{vb}} = {} & \tfrac{1}{2}\{\varphi_a^2(1)\,\varphi_b^2(2) + \varphi_a^2(2)\,\varphi_b^2(1) + 2\varphi_a(1)\,\varphi_b(1)\,\varphi_a(2)\,\varphi_b(2)\} \\ & \times\tfrac{1}{2}\{\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)\}^2\,.\end{aligned}$$

Hence,

$$\begin{aligned}\Gamma(1,2;1,2)_{\mathrm{mo}} = {} & \tfrac{1}{2}\,\Gamma(1,2;1,2)_{\mathrm{vb}} + \tfrac{1}{4}\{\varphi_a^2(1)\,\varphi_a^2(2) + \varphi_b^2(1)\,\varphi_b^2(2) \\ & + 2\varphi_b^2(1)\,\varphi_a(2)\,\varphi_b(2) + 2\varphi_a^2(1)\,\varphi_a(2)\,\varphi_b(2) \\ & + 2\varphi_a^2(2)\,\varphi_a(1)\,\varphi_b(1) + 2\varphi_a(1)\,\varphi_b(1)\,\varphi_a(2)\,\varphi_b(2) \\ & + 2\varphi_a(1)\,\varphi_b(1)\,\varphi_b^2(2)\} \times\tfrac{1}{2}\{\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)\}^2\,.\end{aligned}$$

The atomic terms in Γ_{mo}, which are not present in Γ_{vb}, are given by

$$\tfrac{1}{8}\{\varphi_a^2(1)\,\varphi_a^2(2)+\varphi_b^2(1)\,\varphi_b^2(2)\}\cdot\{\alpha(1)\,\beta(2)-\alpha(2)\,\beta(1)\}^2$$

and give rise to an additional Coulomb term in the expression for the total electronic energy:

$$\tfrac{1}{4}(\varphi_a\varphi_a|\varphi_a\varphi_a)+\tfrac{1}{4}(\varphi_b\varphi_b|\varphi_b\varphi_b)\,. \tag{4}$$

Each term in Eq. (4) can be regarded as originating from the Coulomb interaction between two spin densities of 0.5 associated with each atom.

The analysis is readily generalised for molecular orbital wave functions of many-electron closed shell molecules:

$$\Gamma(1,2;1,2)_{\mathrm{mo}}=\tfrac{1}{2}\{\gamma(1,1)\,\gamma(2,2)-\gamma(1,2)\,\gamma(2,1)\}$$

where

$$\gamma(1,1')=\tfrac{1}{2}\sum_{k,l}P_{kl}\,\varphi_k(1)\,\varphi_l(1')\,\{\alpha(1)\,\alpha(1')+\beta(1)\,\beta(1')\}\,.$$

There atomic term in Γ_{mo}, appropriate to atomic orbital φ_p, is now given by

$$\tfrac{1}{8}P_{pp}^2\,\varphi_p^2(1)\,\varphi_p^2(2)\,\{\alpha(1)\,\beta(2)-\alpha(2)\,\beta(1)\}^2$$

where, once again, the one-centre Coulomb repulsion term originates from the interaction between the two spin densities $\frac{1}{2}P_{pp}$, associated with atomic orbital φ_p.

Thus the valence state energy, defined within the single configuration molecular orbital theory, differs from the corresponding energy derived from the simple valence bond approach, because of the intra-atomic contribution to the diagonal elements of the two-electron density matrix. Terms of this kind would only arise in a more complete valence bond treatment, where covalent and ionic structures, involving doubly occupied atomic orbitals, are explicitly considered. In principle the molecular orbital valence state must be obtained by separating the molecular wave function into its component covalent and ionic structures. Normally this is a very involved procedure and, for practical purposes, some alternative method is required. Two examples are now considered: first the case of H_2, where the valence state energy can be given precisely. Secondly, the case of methane which requires a different treatment.

The valence state energy of hydrogen in H_2 is given by

$$E_{\mathrm{VSMO}}=\langle\varphi_{1s}|-\tfrac{1}{2}\,\nabla^2-\tfrac{1}{r}|\varphi_{1s}\rangle+\tfrac{1}{4}(\varphi_{1s}\,\varphi_{1s}|\varphi_{1s}\,\varphi_{1s})=f+\tfrac{1}{4}\,\delta_{\mathrm{H}}\,.$$

Since $E(\mathrm{H}^-)=2f+\delta_{\mathrm{H}}$, $E(\mathrm{H})=f$, E_{VSMO} can be written unambiguously in terms of the energies of H and H^-:

$$E_{\mathrm{VSMO}}=\tfrac{1}{2}\,E_{\mathrm{H}}(1s,\,{}^2S)+\tfrac{1}{4}\,E_{\mathrm{H}^-}(1s^2,\,{}^1S)=w_{\mathrm{PP}}+\delta_{\mathrm{H}}$$

where w_{PP} is the valence state energy as given by the perfect pairing model.

For carbon in methane, the valence state energy is given by

$$\begin{aligned}&4P_{te_1te_1}f+6P_{te_1te_1}P_{te_2te_2}\cdot\delta'_c+(P_{te_1te_1})^2\cdot\delta_c\\&\quad+12\,P_{te_1te_2}\langle te_1|-\tfrac{1}{2}\,\nabla^2+V_{\mathrm{core}}|te_2\rangle+\tfrac{1}{2}\sum_{\substack{i,j,p,q\\(i\neq j;\;p\neq q)}}P_{te_ite_j}P_{te_pte_q}\\&\qquad[(te_i\,te_j|te_p\,te_q)-\tfrac{1}{2}(te_ite_q|te_pte_j)]\end{aligned} \tag{5}$$

where
$$f=\langle te_1|-\tfrac{1}{2}\nabla^2+V_{\text{core}}|te_1\rangle\,,$$
$$\delta'_c=\{(te_1\,te_1|te_2\,te_2)-\tfrac{1}{2}(te_1\,te_2|te_2\,te_1)\}\,,$$
$$\delta_c=(te_1\,te_1|te_1\,te_1)\,,$$

and te_i ($i=1,2,3,4$) label the tetrahedral hybrid atomic orbitals. If $P_{te_i te_i}=1$, the carbon atom carries no net effective charge, and Eq. (5) reduces to the simpler expression

$$\begin{aligned} &w_{\text{PP}}+\delta_c+12P_{te_1 te_2}\langle te_1|-\tfrac{1}{2}\nabla^2+V_{\text{core}}|te_2\rangle \\ &\quad+\tfrac{1}{2}\sum_{\substack{i,j,p,q\\(i\neq j;\,p\neq q)}} P_{te_i te_j}P_{te_p te_q}[(te_i te_j|te_p te_q)-\tfrac{1}{2}(te_i te_q|te_p te_j)]\,. \end{aligned} \tag{6}$$

The partitioning of the valence state energy implied by Eq. (6) is convenient, and not unique; but it is hoped that any inaccuracies arising from this choice will be marginal.

The Practical Use of Molecular Orbital Valence States

The discussion given in the previous section is now developed to show how Coulomb integrals may be calculated for an atom X, which is involved in the formation n bonds, e.g., as in XY_n. The analysis is then worked through in detail for tetrahedrally co-ordinated boron and nitrogen atoms, as found in cubic boron nitride.

The main difficulty in any extended Hückel molecular orbital calculation arises from the variation of orbital charge density, and hence atomic valence state energy, with each interaction of the self-consistent procedure. It is therefore necessary to find an approximate expression for the valence state energy in terms of the intra-atomic elements of the charge density-bond order matrix $\boldsymbol{P}$. This situation has been recognised by other authors, notably Klopman [10], Oleari and coworkers [11], Ferreria [12, 13], and Jørgensen [14]. But the present work differs from these treatments in the manner in which the one-centre Coulomb integrals are incorporated into the valence state energies. The absence of these terms from conventional treatments has also been noted recently by Joy and Silverstone [15], and Ferreria [16].

For present purposes, it is convenient to describe the bonding in a molecule XY_n in terms of n equivalent (hybrid) atomic orbitals associated with atom X, each one of which is preferentially directed towards a single Y atom. The molecular orbitals are subjected to a unitary transformation in order to yield equivalent molecular orbitals, which are predominantly localised within the X–Y bonding regions. A further simplification is now made whereby the equivalent molecular orbitals are assumed completely localised within the region of a particular X–Y bond. This approximation makes the valence state energy independent of terms depending upon intra-atomic bond orders: an assumption invariably made by other authors without further comment.

The molecular orbital valence state energy, associated with atom X, therefore follows from the generalisation of Eq. (5) to the case of n equivalent orbitals:

$$E_{\text{x}}(P)=n\,P_{\text{x}}\,f+\frac{n(n-1)}{2}\,P_{\text{x}}^2\cdot\delta'_{\text{x}}+\frac{1}{4}\,n\,P_{\text{x}}^2\cdot\delta_{\text{x}}=n\,P_{\text{x}}\alpha_{\text{x}}\,, \tag{7}$$

where $\overline{\alpha}_x$ is the Coulomb integral arising when the total energy is additively partitioned [17]. Alternatively, Eq. (7) may be written in the form [10]:

$$E_x = aq + bq^2 \tag{8}$$

where $a = f$, $b = \dfrac{n-1}{2n}\delta'_x + \dfrac{\delta_x}{4n}$, and q is the valence electron population of atom X.

The Coulomb integral α_x is obtained from Eq. (7) in the manner described in [17]:

$$\alpha_x = f + \left[(n-1)\,\delta'_x + \frac{\delta_x}{2}\right] P_x = a + 2bq\,.$$

The same result is also obtained by differentiating Eq. (8) with respect to q [10].

Thus, on selecting values of q corresponding to X^+, X^0 and X^-, it is not difficult to show that α_x is given by

$$\alpha_x = -\tfrac{1}{2}(I_x^0 + E_x^0) - Q_x(I_x^0 - E_x^0)\,.$$

Q_x is the effective atom charge on atom X, equal to $Z_x - q$, where Z_x is the number of valence electrons provided by X; I_x^0 and E_x^0 are the valence state ionisation potential and electron affinity associated with the processes:

$$X(\varphi_1^{Z_x/n}\,\varphi_2^{Z_x/n}\,\dots\,\varphi_n^{Z_x/n}) \rightarrow X^{\pm}(\varphi_1^{(Z_x\mp 1)/n}\,\varphi_2^{(Z_x\mp 1)/n}\,\dots\,\varphi_n^{(Z_x\mp 1)/n})\,.$$

It now remains to determine I_x^0 and E_x^0 for the particular system under study. In the present paper, the theory will be applied to the calculation α_x for tetrahedrally coordinated boron and nitrogen atoms, as found in the diamond-like modification of boron nitride. The results were recently used without giving a detailed derivation [17].

Determination of I_x^0 and E_x^0 from Spectroscopic Data

I_x^0 and E_x^0 are determined by the energies of the following processes for the boron atom:

$$\begin{aligned} &B(te^{3/4}te^{3/4}te^{3/4}te^{3/4}) \rightarrow B^+(te^{2/4}te^{2/4}te^{2/4}te^{2/4})\,,\\ &B(te^{3/4}te^{3/4}te^{3/4}te^{3/4}) \rightarrow B^-(te^{4/4}te^{4/4}te^{4/4}te^{4/4})\,. \end{aligned} \tag{9}$$

The total energies of the neutral and ionic species, with configurations as given in Eq. (9), are first referred to the energy of the lowest spectroscopic state of the respective species as zero of energy. The problem then reduces to one of calculating promotion energies, providing the lowest energy ionisation potential and electron affinity of boron are available from experiment.

First of all consider the promotion energy associated with the neutral atom. The energy of the boron atom in the configuration given in Eq. (9), follows from Eq. (7):

$$E_B[B(te^{3/4}te^{3/4}te^{3/4}te^{3/4})] = 3f + \tfrac{9}{16}\cdot\delta_B + \tfrac{27}{8}\cdot\delta'_B\,.$$

Instead of working out the promotion energies from first principles, it is more helpful to use the data already compiled by Hinze and Jaffé [18]. However, it should be noted that these data are not suitable, without further modification, for incorporating into generalised Hückel calculations, because of the omission of the single-centre two-electron integrals. The energies of two different configurations of the neutral boron atom are as follows (electrons having random spins):

$$\begin{aligned} E[\mathrm{B}(te\,te\,te)] &= 3\,\mathrm{f} + 3\delta'_{\mathrm{B}} \\ E[\mathrm{B}(te^2\,te)] &= 3\,\mathrm{f} + \delta_{\mathrm{B}} + \delta'_{\mathrm{B}} \end{aligned}$$

The promotion energies for these configurations are listed in Ref. [18]. Thus the promotion energy required in the present work is obtained in the following manner:

$$P[\mathrm{B}(te^{3/4}\,te^{3/4}\,te^{3/4}\,te^{3/4})] = \tfrac{11}{8}\,P[\mathrm{B}(te\,te\,te)] - \tfrac{3}{8}\,P[\mathrm{B}(te^2\,te)] + \tfrac{15}{16}\,\delta_{\mathrm{B}} \tag{10}$$

P denotes the promotion energy of the appropriate atomic configuration within the round brackets.

The promotion energies for the positive and negative ions are obtained in an analogous way:

$$\begin{aligned} &P[\mathrm{B}^+(te^{2/4}\,te^{2/4}\,te^{2/4}\,te^{2/4})] = \tfrac{3}{2}\,P[\mathrm{B}^+(te\,te)] - \tfrac{1}{2}P[\mathrm{B}^+(te^2)] + \tfrac{3}{4}\,\delta_{\mathrm{B}}\,, \\ &P[\mathrm{B}^-(te^{4/4}\,te^{4/4}\,te^{4/4}\,te^{4/4})] = P[\mathrm{B}^-(te\,te\,te\,te)] + \delta_{\mathrm{B}}\,. \end{aligned} \tag{11}$$

Ideally, δ_{B} should depend upon the state of ionisation of the boron atom. However, as discussed in the last section, the calculations are made tractable by neglecting any variation in δ_{B} with ionicity. On the basis of this assumption, δ_{B} is determined by the energy change in either of the processes given in Eq. (12).

$$\begin{aligned} 2\mathrm{B}(te^2\,te) &\rightarrow \mathrm{B}^+(te^2) + \mathrm{B}^-(te^2\,te^2)\,, \\ 2\mathrm{B}(te\,te\,te) &\rightarrow \mathrm{B}^+(te\,te) + \mathrm{B}^-(te^2\,te\,te)\,. \end{aligned} \tag{12}$$

Thus,

$$\delta_{\mathrm{B}} = I_{at} - E_{at} + P[\mathrm{B}^+(te^2)] + P[\mathrm{B}^-(te^2\,te^2)] - 2P[\mathrm{B}(te^2\,te)] \tag{13}$$

or

$$\delta_{\mathrm{B}} = I_{at} - E_{at} + P[\mathrm{B}^+(te\,te)] + P[\mathrm{B}^-(te^2\,te\,te)] - 2P[\mathrm{B}(te\,te\,te)]\,. \tag{14}$$

I_{at} and E_{at} are the lowest energy ionisation potential and electron affinity, respectively, of the neutral boron atom. All of the quantities defining δ_{B} are listed by Hinze and Jaffé [18], and the most suitable value for this parameter is obtained by taking the arithmetic mean of Eqs. (13) and (14).

Fortunately, small errors in δ_{B} are not very important since both I_{B}^0 and E_{B}^0 involve differences in the promotion energies of the atom and the appropriate ion: it therefore follows from Eqs. (10) and (11) that there is only a small coefficient multiplying δ_{B} in the expressions defining I_{B}^0 and E_{B}^0.

The following data for boron are available from the work of Hinze and Jaffé [18]:

$$\begin{aligned} &P[\mathrm{B}(te^2\,te)] = 9.137\ \mathrm{eV}\,, && P[\mathrm{B}(te\,te\,te)] = 6.586\ \mathrm{eV}\,, \\ &P[\mathrm{B}^+(te^2)] = 12.171\ \mathrm{eV}\,, && P[\mathrm{B}^+(te\,te)] = 8.724\ \mathrm{eV}\,, \\ &P[\mathrm{B}^-(te^2\,te^2)] = 7.225\ \mathrm{eV}\,, && P[\mathrm{B}^-(te^2\,te\,te)] = 5.384\ \mathrm{eV}\,, \\ &P[\mathrm{B}^-(te\,te\,te\,te)] = 3.542\ \mathrm{eV}\,, && \\ &I_{at} = 8.296\ \mathrm{eV}\,, && E_{at} = 0.33\ \mathrm{eV}\,. \end{aligned}$$

Substitution of these values into Eqs. (10, (11), (13) and (14) then yields:

$$\begin{aligned} P[\mathrm{B}(te^{3/4}\,te^{3/4}\,te^{3/4}\,te^{3/4})] &= 14.058\ \mathrm{eV}\,,\\ P[\mathrm{B}^{+}(te^{2/4}\,te^{2/4}\,te^{2/4}\,te^{2/4})] &= 13.747\ \mathrm{eV}\,,\\ P[\mathrm{B}^{-}(te^{4/4}\,te^{4/4}\,te^{4/4}\,te^{4/4})] &= 12.537\ \mathrm{eV}\,, \end{aligned}$$

and $\delta_{\mathrm{B}} = 8.995$ eV. I_0^{B} and E_{B}^0 are then obtained from Eq. (9) as

$$I_{\mathrm{B}}^0 = 7.985\ \mathrm{eV} \quad \text{and} \quad E_{\mathrm{B}}^0 = 1.851\ \mathrm{eV}\,.$$

Hence the Coulomb integral for boron has the following dependence upon the effective atomic charge, Q_{B}:

$$\alpha_{\mathrm{B}}\,(\mathrm{eV}) = -4.918 - 6.134\,Q_{\mathrm{B}}\,.$$

The appropriate valence state ionisation potential and electron affinity for the nitrogen atom are determined from the following processes:

$$\mathrm{N}(te^{5/4}\,te^{5/4}\,te^{5/4}\,te^{5/4}) \rightarrow \mathrm{N}^{+}(te^{4/4}\,te^{4/4}\,te^{4/4}\,te^{4/4})$$

$$\mathrm{N}(te^{5/4}\,te^{5/4}\,te^{5/4}\,te^{5/4}) \rightarrow \mathrm{N}^{-}(te^{6/4}\,te^{6/4}\,te^{6/4}\,te^{6/4})\,.$$

The promotion energies for the neutral and ionic species are found by the same procedure which was used above for the boron atom:

$$\begin{aligned} P[\mathrm{N}(te^{5/4}\,te^{5/4}\,te^{5/4}\,te^{5/4})] &= \tfrac{11}{8}\,P[\mathrm{N}(te^2\,te\,te\,te)] - \tfrac{3}{8}\,P[\mathrm{N}(te^2\,te^2\,te) + \tfrac{15}{16}\,\delta_{\mathrm{N}}\,,\\ P[\mathrm{N}^{+}(te^{4/4}\,te^{4/4}\,te^{4/4}\,te^{4/4})] &= P[\mathrm{N}^{+}(te\,te\,te\,te)] + \delta_{\mathrm{N}}\,,\\ P[\mathrm{N}^{-}(te^{6/4}\,te^{6/4}\,te^{6/4}\,te^{6/4})] &= \tfrac{3}{2}\,P[\mathrm{N}^{-}(te^2\,te^2\,te\,te)] - \tfrac{1}{2}\,P[\mathrm{N}^{-}(te^2\,te^2\,te) + \tfrac{3}{4}\,\delta_{\mathrm{N}}\,. \end{aligned}$$

The value of δ_{N} is found by averaging the energy change for the two processes.

$$\begin{aligned} 2\mathrm{N}(te^2\,te\,te\,te) &\rightarrow \mathrm{N}^{+}(te\,te\,te\,te) + \mathrm{N}^{-}(te^2\,te^2\,te^2)\,,\\ 2\mathrm{N}(te^2\,te^2\,te) &\rightarrow \mathrm{N}^{+}(te^2\,te^2) \quad + \mathrm{N}^{-}(te^2\,te^2\,te^2)\,. \end{aligned}$$

Hinze and Jaffé [18] list the following data for nitrogen:

$$\begin{array}{rlrl} P[\mathrm{N}(te^2\,te^2\,te)] & = 14.265\ \mathrm{eV}\,, & P[\mathrm{N}(te^2\,te\,te\,te)] & = 9.920\ \mathrm{eV}\,,\\ P[\mathrm{N}^{+}(te^2\,te^2)] & = 19.104\ \mathrm{eV}\,, & P[\mathrm{N}^{+}(te\,te\,te\,te)] & = 9.524\ \mathrm{eV}\,,\\ P[\mathrm{N}^{-}(te^2\,te^2\,te^2)] & = 8.898\ \mathrm{eV}\,, & P[\mathrm{N}^{-}(te^2\,te^2\,te\,te)] & = 5.818\ \mathrm{eV}\,,\\ I_{at} & = 14.535\ \mathrm{eV}\,, & E_{at} & = 0.05\ \mathrm{eV}\,. \end{array}$$

and δ_{N} is found to have the value 13.512 eV.

Thus $I_{\mathrm{N}}^0 = 16.620$ eV, $E_{\mathrm{N}}^0 = 6.589$ eV and the variation of Coulomb integral with effective charge is given by

$$\alpha_{\mathrm{N}}\,(\mathrm{eV}) = -11.604 - 10.031\,Q_{\mathrm{N}}\,.$$

Conclusion

The general concept of an atomic valence state has been examined within the framework of simple molecular orbital theory. A basic difference between the restricted forms of molecular orbital and valence bond valence states emerges, which can be characterised by the presence of one-centre Coulomb terms in the molecular orbital valence state energy. The recognition of this general feature is essential when performing calculations of the extended Hückel variety. The effect may also be important in other π-electron calculations where the σ bonds are always implicitly described within the perfect pairing formalism.

Calculations of an approximate nature are made for tetrahedrally coordinated nitrogen and boron, as found in cubic boron nitride. The importance of the one-centre Coulomb terms is apparent on comparing the results with those previously obtained by Coulson, Rèdei and Stocker [19]. These authors used an improperly defined valence state, and there is a marked difference with the present work in the predicted variation of Coulomb integral with effective atomic charge.

A more detailed analysis of simple molecular orbital calculations requires the removal of the assumption of complete localisation of the equivalent orbitals: this necessarily involves the recognition of intra-atomic bond orders in the expression for the Coulomb integrals. But at this level of treatment, it is probably better to use a Pariser-Parr-Pople or similar scheme, where all important integrals are considered explicitly.

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