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Chemical valence from the two-particle density matrix

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Summary. The two-particle approach to the covalent and ionic valence indices is presented within the restricted and unrestricted Hartree–Fock theories (RHF and UHF). It is based on the analysis of contributions from the two-particle density matrix Γ in the orthogonal atomic orbital (OAO) representation. The atomic and diatomic valence indices are identified with respect to the reference states of separated atoms or ions and their physical interpretation is given. It is found that ionic indices originate from the Coulomb part of Γ, while the covalent indices are related to its exchange part. They are shown to be related to the differences, with respect to the reference state values, of the condensed Γ-matrix elements, measuring a total probability of simultaneously finding two electrons on atoms A and B. An interpretation of a second-order Taylor expansion around the reference states of the proposed electron pair valence indices is given. Illustrative valence diagrams for the two atomic orbital model are presented for both the $A+B$ and $A^- + B^+$ reference limits, and their implications for the bond description are briefly discussed. The valence indices for simple diatomics and polyatomics are generated within the RHF and UHF schemes. The problem of the residual valence in the RHF approach is examined and the RHF predictions for alternative reference states are compared.

Key words: Two-particle density matrix – Covalent valence – Ionic valence

1. Introduction

The concept of valence has been advanced by chemists to quantify in an intuitive way the covalent bonding between atoms in molecules, as opposed to the ionic bonding, for which a separate bond characterization has been introduced. The idea of such a measure of the covalent bond had been originally defined rather vaguely and this prompted a continuous effort to formulate a more precise definition of a valency in quantum chemistry [1, 2]. The most successful of such definitions have been developed in terms of the first-order density matrix of a

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molecule [3–9], giving generally fractional values close to the intuitive chemical valence numbers in standard covalent bond systems [6]. They have been shown to be capable of characterizing a wide range of bonding situations which are encountered in both molecular structures and chemical reactions. Their fractional character often results from the presence of the ionic bond component, with the interatomic charge transfer usually diminishing (increasing) a capability of the net electron donating (accepting) atoms to form the covalent bonds with other atoms. However, a full description of this interplay of the ionic and covalent components in the chemical bond has been hampered by a lack of reliable ionic valence indices, defined within the same theoretical framework as the covalent valence numbers. The present work represents an attempt to fill this gap in the theory of valence, offering a consistent set of covalent and ionic bond indices (atomic and diatomic) formulated within the same theoretical basis provided by the normalization of the two-particle density matrix.

There are conflicting intuitions behind the bond ionicity in chemistry. On one hand, the ionic bond is usually associated with the nonsymmetrical distribution of the electron density difference which characterizes the charge redistribution accompanying the bond formation. An ionic bond index on this basis was proposed by Evarestov and Veryazov [10]. One could call such an approach to the bond ionicity the one-electron perspective. On the other hand, when approaching the subject from the two-electron perspective, a measure of the bond ionicity is provided by relative contributions from the ionic and covalent structures of the overall wavefunction of a molecule, reflecting upon the probabilities of finding two electrons simultaneously on specified atoms. Using the latter perspective one would conclude, therefore, that there is an inherent ionicity even in the symmetric bond, e.g., in H_2. The present treatment is based upon such an approach to the bond ionicity, which immediately points towards the two-particle density matrix $\mathbf{\Gamma}$, as the convenient theoretical background for extracting the relevant electron pair valence numbers. The two-particle density matrix based on nonorthogonal AO's has already been used to define chemical valence in terms of correlations between the fluctuations of the atomic charges around the average populations of atoms in a molecule [9, 11]. The regional fluctuations in the number of electrons (or in electron density) are related to the regional softness parameters [11, 12].

We would also like to remark at this point that valence is a difference phenomenon, measuring changes in the electron "pairings" in a molecule relative to those in the separated atoms/ions limit (SAL). Only with such a reference the amount of charge transfer, a measure of the atom polarization and the covalent valence index are defined. In the present approach we adopt therefore a similar SAL reference state to define the relevant electron pair valence numbers counting electronic pairs, rather than electrons. Specification of the reference states will be given in a later section. In our approach all main valence components and the competition between them appear naturally, so that such effects as, e.g. the saturation of specific valence components, effect of one component upon another, role of lone electronic pairs (covalent-inactive, but ionic-active), can be discussed on the same theoretical basis.

One of our guiding principles will be to preserve in the theoretical development the essence of the definition of the covalent valence by Gopinathan and Jug [6], given by the sum of squares of the density matrix elements corresponding to pairs of orbitals centered on different atoms, be it in a novel framework. This diagonal quadratic form clearly indicates a two-electron (electron pairing) character of this quantity, conceptually close to the classical Lewis viewpoint of covalent bonds as shared electron pairs. It should be emphasized that it is not generally possible to directly associate with the valence indices also energetical effects. Rather, this concept should be treated as a description of the electron pairing situation change in a molecule, relative to the SAL, providing a supplementary information to energetical considerations. This general attitude has been adopted in the present work: The reported numbers reflect upon changes in two-electron probabilities in a molecule, as revealed by a given Hartree–Fock (HF) ground state wavefunction. The following formalism of chemical valency in terms of changes in finding two electrons on specified atoms is quite general and applies also to correlated wavefunctions. Therefore results based on configuration interaction (CI) could be given at a later time. But the presentation in terms of HF theory contains the basic features and does not impose serious restrictions on the formalism. It is to be understood that HF theory is a many electron theory, despite its usual reduction to molecular orbitals, i.e. one electron functions. Also the effect of left-right correlation is implicitly included in the separated atom reference states which are not HF limit states.

The paper is organized in the following way. In the next section the ionic and covalent valence indices in the RHF and UHF theories are defined. Their physical content and their relation to the differences in the so-called condensed (in atomic resolution) $\boldsymbol{\Gamma}$-matrix elements is the subject of Sect. 3. The problem of residual valence in the RHF scheme is discussed and the corrections to the atomic indices due to a renormalization of the RHF $\boldsymbol{\Gamma}$-matrix in the SAL are proposed. The two-orbital model valency diagrams are the subject of Sect. 4. Finally, the illustrative valence indices for selected diatomics and polyatomics are reported and discussed in Sect. 5, where the effect of alternative choices of the reference atomic configurations is examined in some detail. We adopt the usual AO representation used in the previous development.

2 Two-electron valence contributions

2.1 Summary of basis definitions and relations

Consider the two-particle density matrix [9] in the HF approximation in the orthogonalized atomic orbital (OAO) representation. It can be expressed within RHF theory in terms of the familiar charge-and-bond-order or one-particle density matrix:

$$\boldsymbol{P} = 2\boldsymbol{C}\boldsymbol{C}^{\dagger}$$

where $\boldsymbol{C}$ is the LCAO MO matrix in terms of the OAO basis set $\boldsymbol{\lambda}$. The UHF theory defines separate one-particle density matrices for the occupied MO's associated with the α- and β-spins, respectively:

$$\boldsymbol{P}^{\alpha} = \boldsymbol{C}^{\alpha}\boldsymbol{C}^{\alpha\dagger} \tag{2a}$$

$$\boldsymbol{P}^{\beta} = \boldsymbol{C}^{\beta}\boldsymbol{C}^{\beta\dagger} \tag{2b}$$

giving rise to the total density matrix, $\boldsymbol{P} = \boldsymbol{P}^{\alpha} + \boldsymbol{P}^{\beta}$. In what follows we assume that the basis set includes natural hybrid orbitals (NHO's) of the constituent atoms/ions which diagonalize the atomic blocks of the relevant density matrices in the SAL. This approach was first suggested by McWeeny [13] and more recently adopted by Weinhold and coworkers [14–15] for construction of Lewis structures and characterization of lone pairs and multiple bonds.

The independent-particle approach of the HF theory allows one to factorize the elements of the spinless two-particle density matrix (we adopt the Löwdin [16] normalization):

$$\Gamma(\boldsymbol{r}'_1, \boldsymbol{r}'_2, \boldsymbol{r}_1, \boldsymbol{r}_2) = \binom{n}{2} \int \Psi^*(\boldsymbol{r}'_1, \boldsymbol{r}'_2, \boldsymbol{x}) \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{x})\, d\boldsymbol{x}$$

$$= \sum_{\mu\nu\varrho\sigma}^{OAO} \Gamma(\mu\varrho \mid \nu\sigma) \lambda^*_\mu(\boldsymbol{r}'_1) \lambda_\nu(\boldsymbol{r}_1) \lambda^*_\varrho(\boldsymbol{r}'_2) \lambda_\sigma(\boldsymbol{r}_2) \tag{3}$$

$$\Gamma^{RHF}(\mu\varrho \mid \nu\sigma) = \tfrac{1}{4}(2P_{\mu\nu}P_{\varrho\sigma} - P_{\mu\sigma}P_{\varrho\nu}) \tag{4a}$$

$$\Gamma^{UHF}(\mu\varrho \mid \nu\sigma) = \tfrac{1}{2}(P_{\mu\nu}P_{\varrho\sigma} - P^{\alpha}_{\mu\sigma}P^{\alpha}_{\varrho\nu} - P^{\beta}_{\mu\sigma}P^{\beta}_{\varrho\nu}) \tag{4b}$$

where n is the number of electrons. The pair-diagonal elements, $\Gamma(\mu, \varrho) \equiv \Gamma(\mu\varrho \mid \mu\varrho)$:

$$\Gamma^{RHF}(\mu, \varrho) = \tfrac{1}{4}(2P_{\mu\mu}P_{\varrho\varrho} - P^2_{\mu\varrho}) \tag{5a}$$

$$\Gamma^{UHF}(\mu, \varrho) = \tfrac{1}{2}[P_{\mu\mu}P_{\varrho\varrho} - (P^{\alpha}_{\mu\varrho})^2 - (P^{\beta}_{\mu\varrho})^2] \tag{5b}$$

have the well-known probability interpretation. Namely, they measure in terms of the electronic pairs, the probability of simultaneously finding one electron on λ_μ and another electron on λ_ϱ, for the arbitrary distribution of the remaining electrons. Using the appropriate idempotency relations:

$$\boldsymbol{P}^2 = 2\boldsymbol{P} \quad \text{(closed shell)}$$

$$(\boldsymbol{P}^{\alpha})^2 = \boldsymbol{P}^{\alpha}, \qquad (\boldsymbol{P}^{\beta})^2 = \boldsymbol{P}^{\beta} \quad \text{(open shell)} \tag{6}$$

one immediately verifies that $\boldsymbol{\Gamma} = \{\Gamma(\mu, \varrho)]$ is indeed "normalized" to the number of distinct electronic pairs (see Eq. (3)) in a molecule:

$$\sum_{\mu, \varrho}^{OAO} \Gamma(\mu, \varrho) \equiv \mathrm{Tr}\,\boldsymbol{\Gamma} = n(n-1)/2 \tag{7}$$

This basic relation can be rewritten in terms of the corresponding condensed $\boldsymbol{\Gamma}$-matrix elements:

$$\Gamma(A, B) \equiv \sum_{a}^{A} \sum_{b}^{B} \Gamma(a, b) \tag{8}$$

$$\mathrm{Tr}\,\boldsymbol{\Gamma} = \sum_{A} \sum_{B} \Gamma(A, B) = n(n-1)/2 \equiv \mathcal{N} \tag{7a}$$

In Eq. (8) a denotes an OAO associated with atom A and b an OAO of atom B, respectively. Since $\Gamma(a, b)$ is symmetric, $\Gamma(A, B)$ is also symmetric. Clearly, the respective condensed two electron probabilities:

$$\mathscr{P}(A \mid B) \equiv \frac{1}{\mathcal{N}} \Gamma(A, B)(2 - \delta_{AB}) \tag{9}$$

of simultaneously finding two electrons, one on atom A and another on atom B, for arbitrary distributions of remaining electrons, are then normalized to unity.

$$\sum_{A \leqslant} \sum_{B} \mathscr{P}(A \mid B) = 1 \tag{7b}$$

The closed-shell relations (see Eq. (6)):

$$\begin{gathered}\operatorname{Tr} \boldsymbol{P}^2 = 2 \operatorname{Tr} \boldsymbol{P} = 2n \\ \sum_{\nu \neq \mu} P^2_{\mu\nu} = 2q_\mu - q^2_\mu\end{gathered} \tag{10}$$

where $q_\mu = P_{\mu\mu}$ stands for the orbital occupancy, are fundamental for the previous covalent valence concepts [3–6]. As defined by Gopinathan and Jug [6] the measure of the interatomic covalent bonding extended from an OAO a on A to all other atoms is:

$$V_a = \sum_{B \neq A} \sum_{b}^{B} P^2_{ab} \tag{11}$$

giving rise to the total atomic covalent valency number:

$$V_A = \sum_{a}^{A} V_a \equiv \sum_{B \neq A} V_{AB} \tag{12}$$

and the overall number of covalent bonds in the system in question:

$$M = \tfrac{1}{2} \sum_{A} V_A = \sum_{A \leqslant} \sum_{B} V_{AB} \tag{13}$$

In Eqs. (12) and (13) V_{AB} denotes the interatomic valence number of bond valence:

$$V_{AB} = \sum_{a}^{A} \sum_{b}^{B} P^2_{ab} \tag{14}$$

The intraatomic part of Eqs. (10) has been eliminated in the previous development as reflecting upon the atomic "valence states", rather than "bonding".

The association of the valency concepts with idempotency relations (10) attributes to them a misleading one-electron interpretation. Namely, as it follows from the first Eq. (10) a partitioning of the squares of the density matrix elements (l.h.s.) amounts to a division of the global number of electrons (r.h.s.). This "counting of electrons" via different valence numbers is a somewhat inappropriate context for the concept usually associated in chemistry with electronic pairs shared by the bonding partners. However, as we have observed in Eqs. (5), the products of the density matrix elements $\Gamma(\mu, \varrho)$ appear naturally in the normalization equation (7) of the two-electron density matrix elements appearing now with the l.h.s. representing a partitioning of distinct electronic pairs in the system. We next propose the use of Eq. (7) as the vehicle for extracting the set of useful electron-pair, intra- and interatomic valence indices, characterizing both the covalent and ionic bond components; they represent a more detailed "counting of electronic pairs", measuring changes in the electron pairing situation in a molecule, relative to the SAL.

2.2 Valence contributions and their normalization

To obtain relevant valence numbers, we shall remove from both sides of Eq. (7) all the terms, denoted by 0, relating only to the separated atoms. These are characterized by the relevant OAO occupations:

$$\begin{aligned}\boldsymbol{q}^0 &= \{q^0_\mu\} \quad \text{RHF} \\ \boldsymbol{q}^0 &= [(q^0_\mu)^\alpha, (q^0_\mu)^\beta] \quad \text{UHF}\end{aligned} \tag{15}$$

and the associated atomic populations:

$$\boldsymbol{n}^0 = \{n_A^0\}$$

$$n_A^0 = \sum_{\mu}^{A} q_{\mu}^0 \quad \text{RHF} \tag{16}$$

$$n_A^0 = \sum_{\mu}^{A} [(q_{\mu}^0)^{\alpha} + (q_{\mu}^0)^{\beta}] \quad \text{UHF}$$

We therefore express the current orbital occupations and atomic populations in terms of the relevant reference data of the separated atoms and the corresponding changes in the global orbital occupations in a molecule:

$$\begin{aligned} \boldsymbol{q} &= \boldsymbol{q}^0 + \Delta\boldsymbol{q} \\ \boldsymbol{n} &= \boldsymbol{n}^0 + \Delta\boldsymbol{n} \end{aligned} \tag{17}$$

We now insert Eqs. (17) and (5) into Eq. (7) and subtract from both sides the corresponding terms which refer solely to the separated atoms. This procedure defines the residual electron pair valence $\mathscr{R}(\boldsymbol{q}^0)$ of the whole system, which can be partitioned in the following way:

$$\begin{aligned} \mathscr{R}(\boldsymbol{q}^0) &\equiv \sum_{A} V_A^t + \sum_{A<} \sum_{B} V_{AB}^t \\ &\equiv \sum_{A} (V_A^{ion} + V_A^{cov}) + \sum_{A<} \sum_{B} (V_{AB}^{ion} + V_{AB}^{cov}) \\ &\equiv V^{ion} + V^{cov} \equiv (V_{intra}^{ion} + V_{inter}^{ion}) + (V_{intra}^{cov} + V_{inter}^{cov}) \end{aligned} \tag{18}$$

Here V_A^t and V_{AB}^t denote total electron pair valence indices which are composed of intratomic and interatomic contributions, respectively, from the ionic and covalent pairing effects. $\mathscr{R}(\boldsymbol{q}^0)$ is reference dependent in the RHF scheme:

$$\mathscr{R}^{RHF}(\boldsymbol{q}^0) = \tfrac{1}{4} \sum_{A} \sum_{a}^{A} q_a^0 (q_a^0 - 2) \tag{19}$$

and vanishes exactly when the SAL has closed-shell character. The corresponding UHF expression

$$\mathscr{R}^{UHF}(\boldsymbol{q}^0) = \tfrac{1}{2} \sum_{A} \sum_{a}^{A} \{(q_a^0)^{\alpha}[(q_a^0)^{\alpha} - 1] + (q_a^0)^{\beta}[(q_a^0)^{\beta} - 1]\} = 0 \tag{20}$$

vanishes exactly at the SAL.

The specific expressions for the ionic and covalent terms of Eq. (18) are:

I. RHF *theory*:

$$V_A^{ion} = \tfrac{1}{2} \left[\Delta n_A (n_A + n_A^0) - \tfrac{1}{2} \sum_{a}^{A} \Delta q_a (q_a + q_a^0) \right] \tag{21a}$$

$$V_A^{cov} = -\tfrac{1}{2} \sum_{0<}^{A} \sum_{a'}^{A} P_{aa'}^2 \leqslant 0 \tag{21b}$$

$$V_{AB}^{ion} = n_A^0 \, \Delta n_B + n_B^0 \, \Delta n_A + \Delta n_A \, \Delta n_B \tag{21c}$$

$$V_{AB}^{cov} = -\tfrac{1}{2} V_{AB} = -\tfrac{1}{2} \sum_{a}^{A} \sum_{b}^{B} P_{ab}^2 \leqslant 0 \tag{21d}$$

II. UHF *theory*:

$$V_A^{ion} = \tfrac{1}{2}\left\{ \Delta n_A(n_A + n_A^0) - \sum_a^A [\Delta q_a^\alpha(q_a^\alpha + (q_a^0)^\alpha) + \Delta q_a^\beta(q_a^\beta + (q_a^0)^\beta)] \right\} \quad (22a)$$

$$V_A^{cov} = -\sum_{a<}^A \sum_{a'}^A [(P_{aa'}^\alpha)^2 + (P_{aa'}^\beta)^2] \leqslant 0 \quad (22b)$$

$$V_{AB}^{ion} = n_A^0\, \Delta n_B + n_B^0\, \Delta n_A + \Delta n_A\, \Delta n_B \quad (22c)$$

$$V_{AB}^{cov} = -\sum_a^A \sum_b^B [(P_{ab}^\alpha)^2 + (P_{ab}^\beta)^2] \leqslant 0 \quad (22d)$$

As shown in Appendix A the nonvanishing residual valence of Eq. (19) is due to the closed-shell idempotency relation of Eq. (10), which no longer applies in the generally open-shell SAL configurations. This is why $\mathscr{R}(\boldsymbol{q}^0)$ vanishes exactly only for the closed-shell occupations $q_\mu^0 \in \{0, 2\}$. We shall address this problem in more detail in the next section and in Appendix A, where we examine its relation to the normalization of the asymptotic SAL form of the condensed $\boldsymbol{\Gamma}$-matrix, $\boldsymbol{\Gamma}_\infty$. The nonvanishing $\mathscr{R}(\boldsymbol{q}^0)$ indicates that the normalization of $\boldsymbol{\Gamma}_\infty$ has been affected by $-\mathscr{R}(\boldsymbol{q}^0)$, relative to that of Eq. (7a). However, one can easily correct the intraatomic valency indices of the RHF theory to account for the $\boldsymbol{\Gamma}_\infty$-matrix renormalization. This is explicitly done in the next section, where the relations between total valency indices and the differences of the condensed matrix elements, $\Delta\boldsymbol{\Gamma} = \boldsymbol{\Gamma} - \boldsymbol{\Gamma}_\infty$, are explored.

The only contributions explicitly depending on the reference orbital occupations are the intraatomic ionic valence indices:

$$V_A^{ion} \equiv \tfrac{1}{2}[\Delta n_A(n_A + n_A^0) + 2w_A(\boldsymbol{q}_A^0)] \quad (23)$$

with $w_A(\boldsymbol{q}_A^0)$ denoting the reference dependent part given in Eq. (21a). In the RHF approach, where $\boldsymbol{q}^0$ is limited to integral occupations, $R(\boldsymbol{q}^0)$ counts the half occupied OAO's in the SAL, each orbit contributing $-1/4$ (see Appendix A). To guarantee the rotational invariance of the results in polyatomic systems, statistical (fractional) occupations in each atomic open shell have to be assumed within the RHF reference occupations, or they have to be linked to the molecular OAO occupations. In such cases the expression for $\mathscr{R}(\boldsymbol{q}^0)$ becomes more complicated (Appendix A).

Finally it should be observed that all ionic valence numbers of the present development result from the first terms in $\Gamma(\mu, \varrho)$ expressions in Eqs. (5) and the diagonal part of the remaining terms. All these contributions can be classified as "Coulomb" terms, while the remaining terms, giving rise to the covalent valence indices, have "exchange" character [16].

3 General discussion

Consider now the asymptotic atomic form of the one-particle density matrix. In the UHF scheme the $\boldsymbol{P}^\alpha$ and $\boldsymbol{P}^\beta$ matrices become diagonal:

$$(P_{\mu\nu}^\alpha)_\infty = (q_\mu^0)^\alpha \delta_{\mu\nu} \quad \text{and} \quad (P_{\mu\nu}^\beta)_\infty = (q_\mu^0)^\beta \delta_{\mu\nu} \quad (24)$$

The respective condensed $\boldsymbol{\Gamma}$-matrix elements (Eq. (8)):

$$\Gamma(A, A) = \tfrac{1}{2}\left\{ n_A^2 - \sum_a^A \sum_{a'}^A [(P_{aa'}^\alpha)^2 + (P_{aa'}^\beta)^2] \right\} \quad (25a)$$

$$\Gamma(A, B) = \tfrac{1}{2}\left\{ n_A n_B - \sum_a^A \sum_b^B [(P_{ab}^\alpha)^2 + (P_{ab}^\beta)^2] \right\} \quad (25b)$$

then assume the following asymptotic values:

$$\Gamma_\infty(A \mid A) = \tfrac{1}{2}\left\{ (n_A^0)^2 - \sum_a^A [(q_a^0)^\alpha]^2 + [(q_a^0)^\beta]^2) \right\} \tag{26a}$$

$$\Gamma_\infty(A \mid B) = n_A^0 n_B^0 \tag{26b}$$

with (see Appendix A):

$$\mathrm{Tr}\,\mathbf{\Gamma} = \mathrm{Tr}\,\mathbf{\Gamma}_\infty = \mathscr{R}(\boldsymbol{q}^0) = 0$$

Now, taking the differences with respect to the SAL values gives:

$$\Delta\Gamma(A \mid A) \equiv \Gamma(A \mid A) - \Gamma_\infty(A \mid A) = V_A^t = V_A^{cov} + V_A^{ion} \tag{27}$$

$$\Delta\Gamma(A \mid B) \equiv \Gamma(A \mid B) - \Gamma_\infty(A \mid B) = V_{AB}^t = V_{AB}^{cov} + V_{AB}^{ion} \tag{28}$$

thus relating total electron pair valence numbers to the respective differences in the condensed $\mathbf{\Gamma}$-matrix elements.

The same general result follows within the RHF theory when one formally assumes dissociation into closed-shell fragments. However, the theory is not useful in cases of open-shall dissociation.

The contributions in ionic valence numbers have qualitative electrostatic associations. Consider, for example, the RHF V_A^{ion} index which can be rearranged in the form:

$$V_A^{ion} = \tfrac{1}{2}\sum_a^A \Delta q_a\,[(n_A + n_A^0) - \tfrac{1}{2}\,(q_a + q_a^0)] \tag{29}$$

Therefore, each removal of electrons from an orbital in A, relative to the reference occupation, contributes to the negative intraatomic ionic valence, while any addition of electrons to orbitals in A generates the positive contribution. This is in accord with the expected associated changes in the atomic energy per electron since, for instance, when electrons are partly removed from A the remaining electrons on the atom will be more strongly attracted by the less screened nucleus.

Let us now similarly examine the qualitative trends in the interatomic ionic valency index, V_{AB}^{ion}. The first two terms in Eq. (21c) represent the pairing contribution between electrons on one atom A with the effective charge on another atom B. Such terms are associated with the bonding electrostatic interaction energy when $\Delta n_B < 0$ and antibonding interaction energy when $\Delta n_B > 0$. The last term, proportional to changes in electronic populations on both atoms, will have also the negative sign (bonding electrostatic interaction) where there is a charge transfer between the atoms.

As our discussion of the total valency normalization clearly shows, the ionic and covalent indices are mutually connected. The additional valence "degrees of freedom" offered by the present scheme should reveal, be it in a very general "electron pairing" way, the conjugate effects associated with the bond formation, e.g., the competition effects between bond ionicity and covalency or between interatomic and intraatomic valence contributions.

There are several general relations between the bond valency indices. Consider, for example, the RHF indices. A straightforward rearrangement of the relevant definitions shows that the difference (see Eq. (23)):

$$\begin{aligned} V_{inter}^{cov} - V_{intra}^{cov} &= \mathscr{R}(\boldsymbol{q}^0) - \sum_A w_A(\boldsymbol{q}_A^0) \\ &= -\tfrac{1}{2}\left[n + \tfrac{1}{2}\sum_\mu q_\mu^2 \right] \end{aligned} \tag{30}$$

is reference independent. Yet another relation shows that the total interatomic ionic valency is the negative sum of all global (orbital reference independent) parts of the atomic ionic valencies (see Eq. (23)):

$$V^{ion}_{inter} + \tfrac{1}{2} \sum_{A} \Delta n_A (n^0_A + n_A) = 0 \tag{31}$$

We therefore see that the two parts exactly neutralize each other in the global valency normalization. Clearly, since Eq. (7a) is linearly dependent on the ***P*** idempotency relations and the normalization of its trace (Eq. (10)), when adding all diatomic covalent contributions one recovers the overall Wiberg [17] relation (sum of the second equations in Eq. (10)):

$$4V^{cov}_{inter} = \tfrac{1}{4} \sum_{A} \sum_{a}^{A} q_a (q_a - 2) \tag{32}$$

It has been demonstrated previously [6] that the small atomic covalent contributions can be absorbed in other terms, when one uses the local natural hybrid orbitals (NHO's) on atoms, which diagonalize the atomic blocks of the density matrix ***P***. In such a representation $V^{cov}_A = 0$ for all atoms.

4 An illustrative model

Consider a single, fully occupied MO, in the RHF approximation:

$$\psi = (a + \kappa b)/(1 + \kappa^2)^{1/2} \tag{33}$$

consisting of two OAO's $\lambda_a \equiv a$ and $\lambda_b \equiv b$ on atoms A and B, respectively, with the positive parameter $\kappa = 1$ marking a symmetrical bond combination. The corresponding orbital part Ψ_0, of the two-electron wavefunction, $\Psi(1, 2)$:

$$\Psi_0(1, 2) = \frac{1}{(1 + \kappa^2)} \{a(1)a(2) + \kappa^2 b(1)b(2) + \kappa[a(1)b(2) + a(2)b(1)]\} \tag{34}$$

consists of two ionic valence structures, where two electrons are described by the same OAO and two covalent structures, when electrons are assigned to OAO's on different atoms. The relevant elements $\Gamma(\mu, \nu)$ of the condensed **Γ**-matrix are immediately obtained from the familiar superposition principle:

$$\Gamma(a, a) = (1 + \kappa^2)^{-2} = P^2_{aa}/4 \tag{35}$$

$$\Gamma(b, b) = \kappa^4 (1 + \kappa^2)^{-2} = P^2_{bb}/4 \tag{36}$$

$$\Gamma(a, b) + \Gamma(b, a) = \Gamma(A \mid B) = 2\kappa^2 (1 + \kappa^2)^{-2} = \frac{P^2_{ab}}{2} \tag{37}$$

where P_{ab} are the RHF density matrix elements. In such a single MO approximation only one element in (2×2) ***P*** matrix is independent, e.g.,

$$\begin{aligned} P_{bb} &= 2 - P_{aa} \\ P_{ab} &= (P_{aa} P_{bb})^{1/2} \end{aligned} \tag{38}$$

Under assumption of ionic $(A^- + B^+)$ dissociation, the asymptotic properties for a nonsymmetric bond combination for $\kappa < 1$ are:

$$\psi_\infty \to a, \qquad n^0_A = 2, \qquad n^0_B = 0, \quad \text{i.e., } \Psi_{0,\infty}(1, 2) = a(1)a(2) \tag{39}$$

Such a dissociation preserves the closed-shell character of $\Psi_0(1, 2)$ at the SAL, so that the residual valence vanishes. The SAL values of $\Gamma(\mu, \nu)$:

$$\Gamma_\infty(a, a) = 1, \qquad \Gamma_\infty(a, b) = \Gamma_\infty(b, a) = \Gamma_\infty(b, b) = 0$$

allow one to determine the corresponding valence indices from Eqs. (35)–(37) (notice, that in the model $V_A^{cov} = V_B^{cov} = 0$):

$$V_A^{ion} = -\kappa^2(2+\kappa^2)/(1+\kappa^2) = \frac{P_{aa}^2}{4} - 1 < 0 \tag{40}$$

$$V_B^{ion} = \kappa^4/(1+\kappa^2)^2 = \tfrac{1}{4}P_{bb}^2 > 0 \tag{41}$$

$$V_{AB} = V_{AB}^{ion} + V_{AB}^{cov} = 2\kappa^2/(1+\kappa^2)^2 > 0 \tag{42}$$

where

$$V_{AB}^{cov} = -\tfrac{1}{2}P_{ab}^2 = -2\kappa^2/(1+\kappa^2)^2 = -V_{AB} < 0 \tag{43}$$

and hence

$$V_{AB}^{ion} = -2V_{AB}^{cov} > 0 \tag{44}$$

One similarly determines the corresponding expressions for the $(A^+ + B^-)$ closed-shell SAL, natural for $\kappa > 1$. The relevant valency diagram, with contributions plotted as a function of P_{aa}, is shown in Fig. 1a with the solid lines in the left $\kappa < 1$ part showing the trends of the $(A^- + B^+)$ quantities and the solid lines in the right $\kappa > 1$ part corresponding to the $(A^+ + B^-)$ quantities. These valency quantities are continued into the other part of the diagram as broken lines.

The symmetric $\kappa = 1$ case, e.g. H_2, calls for the UHF description, which correctly represents the SAL(A + B). We would like to remark that for such molecules as H_2 or LiH the only stationary energy solution at the equilibrium

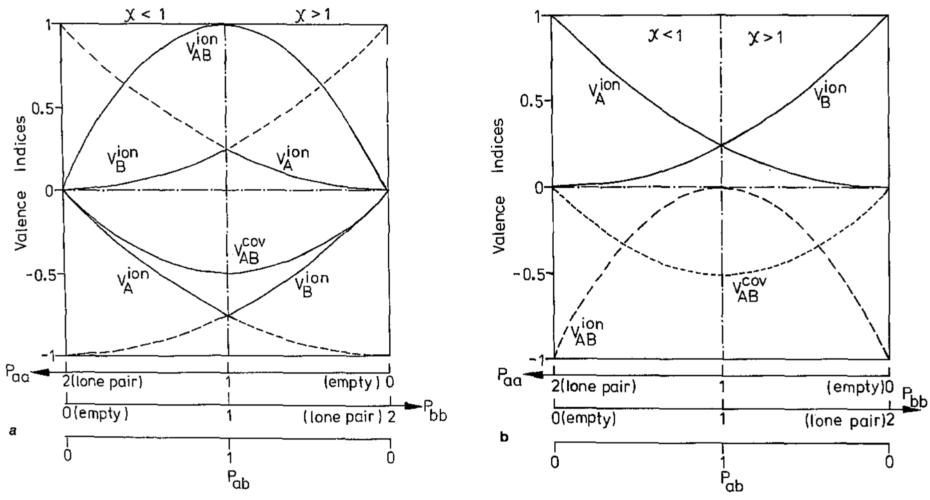

Fig. 1a,b. The electron pair valence diagrams for the 2 OAO model: **a** $(A^- + B^+)$-SAL ($\kappa < 1$, *solid lines*) and $(A^+ + B^-)$-SAL ($\kappa > 1$), *solid lines*) **b** (A + B)-SAL. In part **a** the *solid lines* of one half of the diagram (which defines the reference), and continued as *broken lines* into the other half of the diagram interatomic distance corresponds to the RHF solution, so that both Ψ^{α} and Ψ^{β} MO's are identical. For H_2:

$$P = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \qquad P^{\alpha} = P^{\beta} = \tfrac{1}{2}P$$
$$\Gamma(a, a) = \Gamma(b, b) = 1/4, \qquad \Gamma(A \mid B) = 1/2 \tag{45a}$$

and in the SAL (A + B):

$$P_{\infty} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, P^{\alpha}_{\infty} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, P^{\beta}_{\infty} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$
$$\Gamma_{\infty}(a, a) = \Gamma_{\infty}(b, b) = 0, \qquad \Gamma_{\infty}(A \mid B) = 1 \tag{45b}$$

H_2 achieves maximum covalency at infinite separation, where the wavefunction is totally covalent. Since again the intraatomic valence contributions vanish in the model and by symmetry $\Delta n_A = \Delta n_B = 0$, so that $V^{ion}_{AB} = 0$, one obtains:

$$V^{ion}_{A} = V^{ion}_{B} = 1/4 \quad \text{and} \quad V^{cov}_{AB} = -1/2 \tag{46}$$

This means that the intraatomic ionic contributions are increasing and the covalent contribution is decreasing in the formation of the bond. In the MO picture the bond is 50% covalent and 50% ionic in the H_2 molecule. It should be observed that the magnitudes of these numbers exactly reflect the valence structure composition in Eq. (34) for $\kappa = 1$.

It is also of interest to consider the model valence numbers for the dissociation of the symmetrical bond, e.g. in H_2, into ionic ($A^- + B^-$) products:

$$V^{ion}_{A} = -3/4, \quad V^{ion}_{B} = 1/4, \quad V^{cov}_{AB} = -1/2, \quad V^{ion}_{AB} = 1 \tag{47}$$

This means that the intraatomic ionic valence contribution decreases on atom A and increases on atom B. The interatomic covalent changes are invariant with respect to the reference and are the same as in the case of dissociation into H + H. The interatomic ionic contribution increases by transfer of one electron from atom A to atom B. Notice, that the signs of the atomic contributions are consistent with the equal distribution of electrons in a molecule, which for the assumed reference implies: $\Delta n_A < 0$ and $\Delta n_B > 0$. The indices in Eq. (47) follow from both UHF and RHF descriptions.

Let us finally discuss the UHF description of the interplay between various valence degrees of freedom of the model, when a nonsymmetrical ($\kappa \neq 1$) bond in AB, say LiH, dissociates into atomic products. Again, when the only stationary energy solution corresponds to the RHF orbital, i.e., $P^{\alpha} = P^{\beta} = \frac{1}{2}P$, the relevant expressions for the charge transfer and the nonvanishing valence indices are:

$$\Delta n_A = P_{aa} - 1 = (1 - \kappa^2)/(1 + \kappa^2)^2 = -\Delta n_B = -P_{bb} + 1 \tag{48}$$

$$V^{ion}_{AB} = -(1 - \kappa^2)^2/(1 + \kappa^2)^2 = -\tfrac{1}{4}(P_{aa} - P_{bb})^2 \leqslant 0 \tag{49}$$

$$V^{ion}_{A} = (1 + \kappa^2)^{-2} = \tfrac{1}{4}P^2_{aa} > 0 \tag{50}$$

$$V^{ion}_{B} = \kappa^4/(1 + \kappa^2)^2 = \tfrac{1}{4}P^2_{bb} > 0 \tag{51}$$

$$V^{cov}_{AB} = V^{cov}_{AB} = -\tfrac{1}{2}P^2_{ab} < 0 \tag{52}$$

The corresponding diagram for the (A + B)-SAL is shown in Fig. 1b. The general trends following from Eqs. (49)–(52) are indeed reflected by the

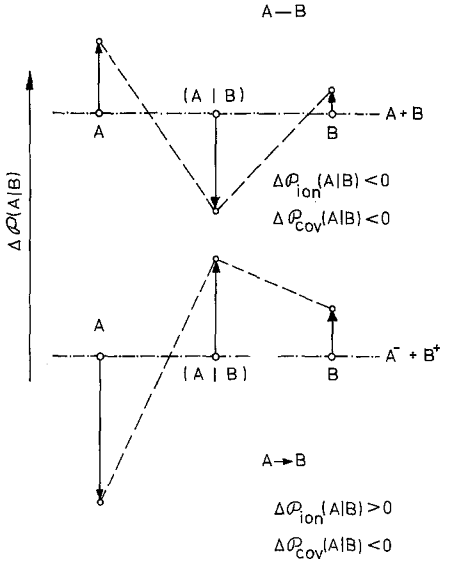

Fig. 2. Qualitative condensed two-electron probability diagrams for diatomic molecules exhibiting a covalent (A – B) and a donor-acceptor (coordination) (A → B) bonds, respecitvely

corresponding SINDO1 [15] results for LiH ($0 < \kappa < 1$) (see Table 1 below):

$$V^{ion}_{\mathrm{H}} = 0.412, \qquad V^{ion}_{\mathrm{Li}} = 0.180, \qquad V^{cov}_{\mathrm{H}} = 0,$$
$$L^{cov}_{\mathrm{Li}} = -0.052, \qquad V^{ion}_{\mathrm{LiH}} = -0.081, \qquad V^{cov}_{\mathrm{LiH}} = -0.460$$

As a final qualitative result we would like to mention the valence indices for H_2^+ relative to the $(\mathrm{A}+\mathrm{B}^+)$-limit:

$$V^{cov}_{A} = V^{cov}_{B} = V^{ion}_{A} = V^{ion}_{B} = 0, \qquad V^{ion}_{AB} = -V^{cov}_{AB} = 1/4$$

As we have already pointed out earlier the sum of all valency contributions for a given atom, or for a pair of atoms, respectively, reflect upon the changes (relative to the SAL reference) in the condensed two-electron probabilities. It follows from Eqs. (49)–(52) (Fig. 1b) that in the case of dissociation into atoms, when the bond can be classified as truly covalent (as opposed to the donor-acceptor bond, associated with the dissociation into ions) A–B:

$$\Delta\mathscr{P}(A \mid A) > 0, \quad \Delta\mathscr{P}(A \mid B) < 0, \quad \Delta P_{ion}(A \mid B) < 0, \quad \Delta\mathscr{P}_{cov}(A \mid B) < 0 \qquad (53)$$

where, in diatomic part:

$$\Delta\mathscr{P}_{ion}(A \mid B) = V^{ion}_{AB}/\mathscr{N} \qquad (53a)$$
$$\Delta\mathscr{P}_{cov}(A \mid B) = V^{cov}_{AB}/\mathscr{N} \qquad (53b)$$

This is qualitatively shown in the upper two-electron probability diagram shown in Fig. 2. A different (lower) diagram results when the bond has a bond-acceptor (coordination) character A ← B. In such a case (see Eqs. (40)–(44) and Fig. 1a):

$$\begin{gathered}\Delta\mathscr{P}(A \mid A) < 0, \qquad \Delta\mathscr{P}(B \mid B) > 0, \qquad \Delta\mathscr{P}(A \mid B) > 0, \\ \Delta\mathscr{P}_{ion}(A \mid B) > 0, \qquad \Delta\mathscr{P}_{cov}(A \mid B) < 0\end{gathered} \qquad (54)$$

Such probability diagrams provide therefore additional bond characteristics, reflecting the "origin" of the electronic pair shared in the bond. One could expect that the present valency indices should provide new classification schemes of various bonding situations in molecular systems.

5 Numerical results and discussion

In this section we shall summarize the illustrative numerical results obtained for a selection of diatomic and polyatomic molecules, generated for various alternative reference occupations in the RHF version. All these results correspond to the dissociation of a molecule into atoms. The relevant density matrices have been obtained from the SINDO1 [18] SCF MO calculations.

5.1 Description of the reference orbital occupations

In order to examine how strongly the assumed reference orbital occupations affect the atomic valence numbers within the RHF scheme several reference configurations have been selected. The first choice involved the standard integral occupations, with the $2s^1 2p^3$ configuration being assumed for the carbon atom and the OAO density matrix $\boldsymbol{P}$

Reference I:

$$\boldsymbol{q}_A^0 = \{n_{lA}\} \quad \text{and} \quad \boldsymbol{P} \tag{55}$$

where n_{lA} is the occupation number of shell l of atom A. For carbon it holds that $\boldsymbol{q}_A^0 = \{1, 3\}$. To assure the necessary invariance properties it would be desirable to link the orbital occupations to molecular density matrix $\boldsymbol{P}$, via an appropriate $\boldsymbol{q}^0 = \boldsymbol{q}^0(\boldsymbol{P})$ relation. The simplest choice, and this is the second reference used in the present RHF study, is a simple scaling of all diagonal elements q_μ corresponding to an atom A, i.e. $\boldsymbol{q}_A$ by a common scaling factor, $\zeta_A = n_A^0/n_A$.

Reference II:

$$\boldsymbol{q}_A^0 = \boldsymbol{q}_A \zeta_A \quad \text{and} \quad \boldsymbol{P} \tag{56}$$

Such a procedure preserves proportions between OAO occupations in their molecular valence state and provides realistic approximations to orbital occupations of atoms in the polarized (promoted) state (before charge transfer). The additional rationale for such a procedure is our goal of removing from the valency quantities all terms exclusively reflecting the intraatomic charge rearrangements, associated with exciting (promoting) the constituent atoms to their hypothetical polarized states. The associated "promotion energy", while affecting the relevant activation energy of the bond formation reaction, should have little effect on the reaction energy, i.e. the bond strength of which the valency is a supplementary, "electron pairing" characteristics.

Yet another choice of the reference atomic occupations, which links them with the molecular orbital density matrix, is associated with the NHO's [10]:

$$\boldsymbol{\phi}_A = \boldsymbol{\lambda}_A \boldsymbol{U}_A \tag{57}$$

which diagonalize the atomic blocks $\boldsymbol{P}_{AA}$ of $\boldsymbol{P}$:

$$\boldsymbol{P}'_A = \tilde{\boldsymbol{U}}_A \boldsymbol{P}_{AA} \boldsymbol{U}_A, \qquad (P'_A)_{rs} = P'_{A,r}\delta_{rs} \tag{58}$$

where $\{P'_{A,r}\}$ groups the NHO occupation in A. This local hybridization of OAO's influences neither V^{cov}_{inter} nor V^{ion}_{inter} (and their diatomic contributions), and it totally absorbs $(V^{cov}_{intra}) = (V^{cov}_A) = \cdots = 0$ into the (V^{ion}_{intra}) term, again with only its first term, $w(\boldsymbol{q}^0)$, being affected. We would like to observe, however, that the

NHO occupations have to be scaled back to the initial atomic electron populations in order to reflect orbital occupations before charge transfer.

Reference III:

$$\boldsymbol{q}_A^0 = \boldsymbol{P}'_A \zeta_A \quad \text{and} \quad \boldsymbol{P} \tag{59}$$

Obviously, the choice of the reference AO occupations does not have to be linked to the representation of the density matrix. Therefore, a possible scheme IV of determining valence indices may involve the NHO density matrix, $\boldsymbol{P}'$, and the reference atom occupations with statistical distribution of electrons in each open shell in the SAL.

Reference IV:

$$\boldsymbol{q}_A^0 = \{n_{lA}^0/m_l\} \quad \text{and} \quad \boldsymbol{P} \tag{60}$$

where n_{lA}^0 denotes the number of electrons of shell l of A in the SAL, and m_l stands for the orbital degeneracy of shell l.

In the UHF calculations the ground state configurations in the SAL have been assumed.

The RHF atomic valence numbers for selected diatomics and polyatomics are compared in Table 1. The corresponding UHF atomic data are collected in Table 2. In Table 2 we have also collected the relevant diatomic indices, common to both HF schemes. The reported RHF data have been obtained from Eqs. (21), so that they exhibit the residual valence whenever the open shells are involved in the SAL.

5.2 Model predictions

It follows from Fig. 1a that the extreme, separated ions [$A^- + B^+(P_{aa} = 2, \kappa = 0)$ and $A^+ + B^-(P_{bb} = 2, \kappa = \infty)$] valency indices are consistent with intuitive predictions: zero covalency, zero diatomic ionic valency, maximum ionic valency of the anion, and vanishing ionic component of the cation. The signs of ionic contributions do indeed reflect the changes in the atomic electronic populations relative to the respective reference state. Namely, in the left part ($0 < \kappa < 1$) atom A is donating electrons to B ($V_A^{ion} < 0$ and $V_B^{ion} > 0$), while the opposite is the case in the right part of the diagram ($\kappa > 1$). The positive values of V_{AB}^{ion} are due to the assumed asymmetry in the reference electron distribution; e.g., for $\kappa = 1$, one of the electrostatic terms vanishes since one atom exhibits a zero reference population and the remaining positive electrostatic contribution is twice the magnitude of the negative $\Delta n_A\, \Delta n_B$ term. The shift of the diatomic ionic index in Fig. 1b, by -2 relative to Fig. 1a diagram, is due to the assumed symmetric distribution of electrons. Now, for V_{AB}^{ion} vanishes exactly ($\kappa = 1$) and assumes the maximum value for the lone pair structures, say $P_{aa} = 2$, with the contributions: $\Delta n_A n_B^0 = +1$, $\Delta n_B n_A^0 = -1$ and $\Delta n_A\, \Delta n_B = -1$.

Both diagrams demonstrate a balance between various ionic and covalent valency parts in a model. In Fig. 1b the maximum covalency is reached when the atomic valencies are lowered (raised) to a quarter of the lone pair value, and when diatomic ionic valency vanishes. The reported earlier values for LiH with a very low magnitude of V_{HLi}^{ion} indicate that this molecule should be placed in the general region $0 < \kappa < 1$ of the diagram. Here κ is closer to one than to zero.

Table 1. The RHF total atomic valence V_A numbers, the residual valence $\mathcal{R}$, and the atomic electron population n_A and n_B for selected diatomics and polyatomics. (For the diatomic valence indices V_{AB} see Table 2)

References	I			II			III			IV				
AB_n	V_A	V_B	$\mathcal{R}$	V_A	V_B	$\mathcal{R}$	V_A	V_B	$\mathcal{R}$	V_A	V_B	$\mathcal{R}$	n_A	n_B
H_2	0.00	0.00	−0.50	0.00	0.00	−0.50	0.00	0.00	−0.50	0.00	0.00	−0.50	1.00	1.00
HLi	0.16	−0.12	−0.50	0.16	−0.22	−0.60	0.16	−0.12	−0.50	0.16	−0.12	−0.50	1.28	0.72
HF	−0.09	1.32	−0.50	−0.11	1.23	−0.59	−0.09	1.24	−0.65	−0.09	1.15	−0.67	0.80	7.20
LiF	−0.17	3.69	−0.50	−0.36	3.51	−0.87	−0.31	3.51	−0.82	−0.17	3.53	−0.67	0.45	7.55
CO	−0.78	0.82	−1.50	−0.78	0.82	−1.50	−0.40	0.64	−1.30	−0.44	0.65	−1.33	3.88	6.12
N_2	0.00	0.00	−1.50	0.00	0.00	−1.50	0.00	0.00	−1.50	0.00	0.00	−1.50	5.00	5.00
CO_2	−2.28	2.03	−2.00	−2.23	1.84	−2.33	−2.23	1.89	−2.23	−1.94	1.86	−2.00	3.30	6.35
OLi_2	3.71	−0.06	−1.00	3.47	−0.24	−1.62	3.47	−0.22	−1.58	3.55	−0.06	−1.17	6.62	0.69
NLi_3	3.05	0.01	−1.50	2.86	−0.18	−2.24	2.86	−0.15	−2.16	3.05	−0.01	−1.50	5.62	0.79

Table 2. The UHF valence contributions for selected diatomics and polyatomics ($\mathscr{R} = 0$)

	Atomic						Diatomic						Total		
AB_n	V_A^{ion}	V_B^{ion}	V_A^{cov}	V_B^{cov}	V_A	V_B	V_{AB}^{ion}	$V_{BB'}^{ion}$	V_{AB}^{cov}	$V_{BB'}^{cov}$	V_{AB}	$V_{BB'}$	V^{ion}	n_a	n_B
H_2	0.25	0.25	0.00	0.00	0.25	0.25	0.00	—	−0.50	—	−0.50	—	0.50	1.00	1.00
HLi	0.42	0.18	0.00	−0.05	0.42	0.13	−0.08	—	−0.46	—	−0.54	—	0.51	1.28	0.72
HF	0.16	1.59	0.00	−0.02	0.16	1.57	−1.25	—	−0.48	—	−1.73	—	0.50	0.80	7.20
C_2	0.82	0.82	0.00	0.00	0.82	0.82	0.00	—	−1.63	—	−1.63	—	1.64	4.00	4.00
BN	0.15	1.95	−0.01	−0.02	0.14	1.93	−0.57	—	−1.49	—	−2.06	—	1.52	2.75	5.25
BeO	0.05	3.12	−0.03	−0.03	0.02	3.09	−1.94	—	−1.17	—	−3.11	—	1.22	1.56	6.44
LiF	0.09	3.95	−0.01	−0.01	0.08	3.94	−3.62	—	−0.40	—	−4.02	—	0.42	0.45	7.55
CO	0.34	1.36	−0.11	0.04	0.33	1.32	−0.26	—	−1.29	—	−1.55	—	1.44	3.88	6.12
N_2	0.82	0.82	−0.07	−0.07	0.75	0.75	0.00	—	−1.50	—	−1.50	—	1.65	5.00	5.00
CO_2	−1.28	2.58	0.00	−0.06	−1.28	2.52	−3.06	4.35	−0.94	−0.13	−4.00	4.22	2.11	3.30	6.35
OLi_2	4.21	0.21	0.00	0.01	4.21	0.20	−0.15	−0.53	−0.57	0.04	−2.02	−0.57	1.19	6.62	0.69
NLi_3	3.80	0.28	0.00	−0.02	3.80	0.26	−0.54	−0.37	−0.56	−0.06	−1.10	−0.43	1.91	5.62	0.79

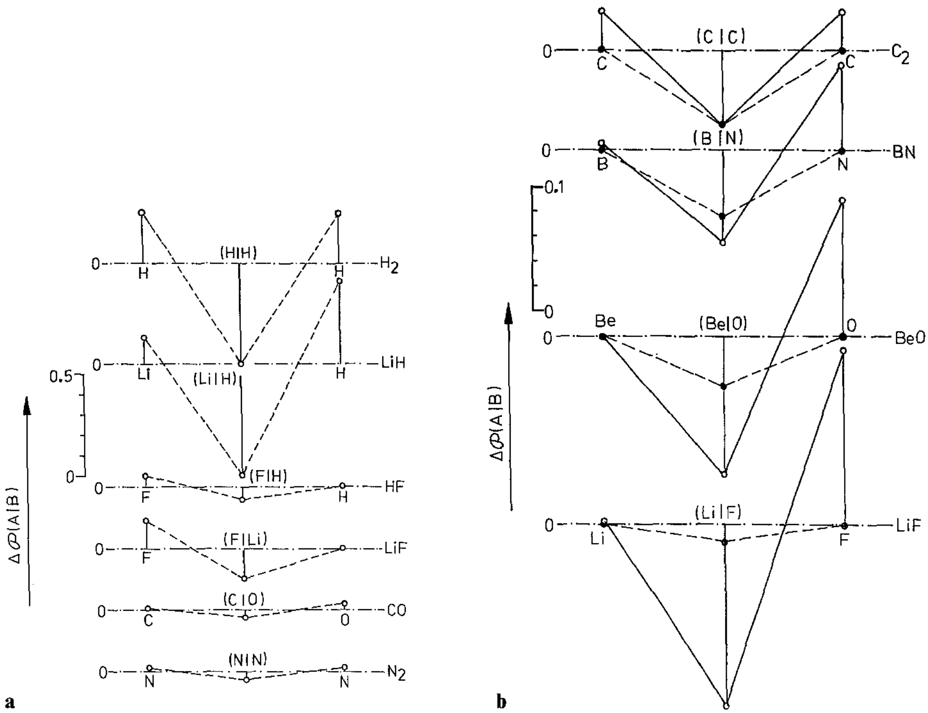

Fig. 3a,b. Quantitative condensed two-electron probability diagram for selected diatomics from the SINDO1 SCF MO calculations: **a** non-isoelectronic systems; **b** isoelectronic systems. In part **b** both total (*solid line*) and covalent (*broken line*) probability changes are shown

Again, the lone pair situation corresponds to the zero covalency and the maximum ionic contribution of the anion, vanishing ionicity of cation, and the maximum magnitude of the charge transfer (diatomic) ionicity. This is an explicit demonstration of the expected charge transfer lowering of the system covalent component of valency. Yet another demonstration of the competition between the covalent and ionic bond components is provided by the ionic covalent partitioning of the condensed probability diagram in Fig. 3b, where isoelectronic molecules with gradually increasing bond ionicity are considered (see the discussion in the following section).

5.3 Probability diagrams

All probability plots of Fig. 3 have a general A–B character of the upper qualitative diagram in Fig. 2. However, with increase of $\mathcal{N}$, the probability changes diminish very strongly. Therefore, one should rather use the valence numbers, instead of the condensed probabilities themselves, as measures of the changes in the two-electron probability distribution in the molecule. One observes in the HF approximation the net decrease of simultaneously finding one electron on A and the other on B and an increase in probability of finding two electrons simultaneously on one atom, relative to the separated atom values. For strongly ionic bonds, e.g., in HF and LiF, one observes an increase in probability on the more electronegative atom, and practically the opposite change in the diatomic probability value, with the more electropositive atom exhibiting almost zero shift in its probability value.

Figure 3b, where we have compared total and covalent condensed probability changes in a series of four isoelectronic molecules, offers additional insight into the covalent versus ionic competition in chemical bonding. The series starts with a pure covalent bonding of a homonuclear diatomic C_2, followed by heteronuclear diatomics with a gradually increasing bond ionicity. In a homonuclear case (the same observation applies to H_2 and N_2 of Fig. 3a) the $\Delta\mathcal{P}(A \mid A) > 0$ is solely due to the ionic contribution $\Delta\mathcal{P}_{ion}(A \mid A) \equiv V_A^{ion}/\mathcal{N}$, since $\Delta\mathcal{P}_{cov}(A \mid A) \equiv V_A^{cov}/\mathcal{N} = 0$, while the $\Delta\mathcal{P}(A \mid B) < 0$ is exactly due to the covalent contribution (53b). With increasing bond ionicity one observes a nonsymmetrical probability diagram with the two-electron probability transfer being observed from the $\mathcal{P}(A \mid B)$ component to the more electronegative atom $\mathcal{P}(A \mid A)$ part. The magnitude of these changes increases with the increasing amount of charge transfer, determined by the relevant electronegativity difference. The increasing bond ionicity is also manifested by the decreasing covalent contribution in the $\mathcal{P}(A \mid B)$ lowering. In the most ionic LiF case it is strongly dominated by the ionic component, which was totally absent in the homonuclear case. The changes in the $\Delta\mathcal{P}(A \mid B)$ contribution parallel the expected changes in the relative contributions of covalent VB structures in the ground-state wavefunction. With increasing bond ionicity the covalent contributions diminish with a simultaneous increase in the participation of the ionic structures of the more electronegative atom (A), and the associate decrease in the presence of the ionic structures associated with a less electronegative atom (B). Since:

$$\Delta\mathcal{P}_{ion} = (n_A n_B - n_A^0 n_B^0)/\mathcal{N}$$

measures the change in the classical (global) pairing number of electrons on constituent atoms, while $\Delta\mathcal{P}_{cov}$ provides a similar measure of the change in the quantum-mechanical (orbital) electron pairing number, one concludes from Fig. 3b that increased bonding ionicity diminishes the contribution of the latter electron pairing change, while increasing the contribution of the former. In a sense bonding becomes more classical when its ionic character increases.

The general trends of the overall $\Delta\mathcal{P}(A \mid B)$ quantities obtained from the present two-electron perspective, viz., diminishing of $\Delta\mathcal{P}(A \mid B)$ and increasing $\Delta\mathcal{P}(A \mid A)$, relative to the atomic dissociation limit, are somewhat surprising in view of familiar intuitions based upon the one-electron perspective, e.g. accumulation of electrons in the bonding region. This apparent contradiction can be explained by again considering the simple two atomic orbital model of Sect. 14. Namely, at the SAL the product wavefunction $\Psi_{0,\infty}(1, 2) = a(1)b(2)$ has exclusively covalent type contribution, which implies $P_\infty(A \mid B) = 1$. When two atoms are forming the chemical bond, the relevant wavefunction (34) divides this probability into atomic ionic and covalent-type two-electron probabilities. This clearly shows that $P(A \mid B)$ has to decrease in the molecule indeed.

5.4 Numerical results

We have used the semiempirical MO method SINDO1 [18] for the calculation of simple molecules to demonstrate the consequences of the valence analysis developed in the previous sections. These calculations are suitable since they give the correct ground state (e.g. BeO) and dipole moment directions (e.g. CO) for

Table 3. Valence differences $\Delta V = V_A - V_B$ for RHF and UHF calculations

	RHF				UHF
AB_n	I	II	III	IV	
H_2	0.00	0.00	0.00	0.00	0.00
HLi	0.38	0.38	0.28	0.28	0.29
HF	−1.41	−1.34	−1.33	−1.24	−1.41
C_2	—	—	—	—	0.00
BN	—	—	—	—	−1.79
BeO	—	—	—	—	−3.07
LiF	−3.86	−3.87	−3.82	−3.70	−3.86
CO	−1.60	−1.60	−1.04	−1.09	−0.99
N_2	0.00	0.00	0.00	0.00	0.00
CO_2	−4.31	−4.07	−4.12	−3.80	−3.80
OLi_2	3.65	3.71	3.69	3.61	4.01
NLi_3	3.04	3.04	3.01	3.04	3.54

all systems considered. We present in Table 1 atomic valence numbers V_A and residual valences $\mathcal{R}$ together with the atomic electron populations n_A.

The residual valence $\mathcal{R}$ is a measure of pairing. It is an indication of the magnitude of open-shell character in the tomic reference frame. Reference I shows that $-2\mathcal{R}$ is the number of bonds that are broken in the unpairing of electron in the atomic reference. This number is 1 for H_2, HLi, HF, LiF, 2 for OLi_2, 3 for CO, N_2, NLi_3, and 4 for CO_2. The results for valence numbers V_A and V_B are very similar in all four reference frames. The negative values indicate usually electron donating atoms, the positive values electron accepting atoms. The values of V_A and V_B are subject to variations in $\mathcal{R}$ and have no absolute meaning.

In Table 2 both atomic and diatomic contributions to UHF valence are listed in the ionic and covalent partitioning scheme advanced in the previous sections. The UHF MO's are the same as the RHF MO's, i.e. pure singlets, not spin contaminated. This means that the RHF solutions are interpreted.

As already shown in Fig. 3a and 3b the isoelectronic series C_2, BN, BeO and LiF shows a competition between interatomic ionic and interatomic covalent valence contributions. A decrease in the bond covalence corresponds to an increase in the bond ionicity. Negative interatomic valence numbers V_{AB}^{cov} are an indication of bonding, so are positive valence numbers V_{AB}^{ion}. These diatomic contributions are independent of the atomic reference and are therefore the same for RHF and UHF.

Finally we have listed the differences $\Delta V = V_A - V_B$ of atomic valence numbers in Table 3. These differences are fairly insensitive with respect to a change of reference. For the isoelectronic series C_2, BN, BeO, LiF they reflect an increase in bond ionicity when going from C_2 to LiF. Again the values should not be considered as relevant in an absolute sense.

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Appendix A: Residual valence and the $\boldsymbol{\Gamma}_\infty$ normalization

As shown in Eq. (31) the nonvanishing residual valence of the RHF valence numbers is due to the open-shell structure of the SAL and is related to the shift of the $\boldsymbol{\Gamma}_\infty$ normalization from that of $\boldsymbol{\Gamma}$, i.e., $\mathcal{N} = n(n-1)/2$:

$$\mathscr{R}(\boldsymbol{q}^0) = \mathcal{N} - \operatorname{Tr} \boldsymbol{\Gamma}_\infty \tag{A1}$$

In order to examine the normalization of the asymptotic $\boldsymbol{\Gamma}$-matrix in more detail we partition the asymptotic density matrix $\boldsymbol{P}_\infty$, into the closed-shell $\boldsymbol{P}_{cs}$, and open-shell $\boldsymbol{P}_{os}$ parts:

$$\boldsymbol{P}_\infty = \boldsymbol{P}_{cs} + \boldsymbol{P}_{os} \tag{A2a}$$

$$\boldsymbol{P}_{cs} = 2\langle \lambda | \hat{P}_{cs} | \lambda \rangle \tag{A2b}$$

$$\boldsymbol{P}_{os} = \sum_{\mu}^{os} q_\mu^0 \langle \lambda | \hat{P}_\mu | \lambda \rangle \equiv \sum_{\mu}^{os} q_\mu^0 \boldsymbol{P}_\mu \tag{A2c}$$

where $\hat{P}_{cs}$ is the projection operator onto the subspace of doubly occupied OAO's and $\{\hat{P}_\mu\}$ are the projectors associated with each OAO partially occupied by q_μ^0 electrons in the SAL. From Eqs. (A2) one immediately obtains:

$$\begin{aligned} \operatorname{Tr} \boldsymbol{P}_\infty^2 &= 2 \operatorname{Tr} \boldsymbol{P}_{cs} + \sum_{\mu}^{os} q_\mu^0 \operatorname{Tr} \boldsymbol{P}_\mu \\ &= 2n_{cs} + \sum_{\mu}^{os} (q_\mu^0)^2 \end{aligned} \tag{A3}$$

where $n_{cs} = n - n_{os}$ is the overall number of electrons in the doubly occupied OAO's of the SAL, and $n_{os} = \sum_\mu^{os} q_\mu^0$. Hence (see Eq. (5a)):

$$\begin{aligned} \operatorname{Tr} \boldsymbol{\Gamma}_\infty &= \tfrac{1}{2}n^2 - \tfrac{1}{2}(n - n_{os}) - \tfrac{1}{4}\sum_{\mu}^{os} (q_\mu^0)^2 \\ &= \mathcal{N} + \tfrac{1}{4}\sum_{\mu}^{os} (2 - q_\mu^0) q_\mu^0 \end{aligned} \tag{A4}$$

which immediately leads, via Eq. (A1), to the RHF residual valency value of Eq. (19).

For the integral OAO occupied in the SAL (reference I):

$$\mathscr{R}(\boldsymbol{q}_A^0) = -n_s/4 \tag{A5}$$

where n_s is the number of singly occupied OAO's. When the statistical distribution of electrons in the open atomic shells is considered (reference IV):

$$\mathscr{R}(\boldsymbol{q}_A^0) = \tfrac{1}{4}\sum_{l}^{os} (q_l^0 - 2) n_l \tag{A6}$$

where n_l is the total number of electrons in the open atomic shell l, and $q_l^0 = n_l/m_l$, where m_l is the shell orbital degeneracy.

The nonvanishing residual valence in the RHF scheme results since the closed-shell idempotency relation (6) no longer applies in the SAL. In the UHF case the open-shell relations (6) apply both in a molecule and in the SAL, thus preserving the $\mathbf{\Gamma}$-matrix normalization and giving rise to the vanishing $\mathscr{R}(\boldsymbol{q}^0)$. Namely, it follows from Eqs. (26) that:

$$\begin{aligned}\operatorname{Tr}\mathbf{\Gamma}_\infty &= \tfrac{1}{2}\left\{n^2 - \sum_A \sum_a^A ([(q_a^0)^\alpha]^2 + [(q_a^0)^\beta]^2)\right\} \\ &= \tfrac{1}{2}\left\{n^2 - \sum_A \sum_a^A [(q_a^0)^\alpha + (q_a^0)^\beta]\right\} = \mathscr{N} = \operatorname{Tr}\mathbf{\Gamma} \qquad \text{(A7)}\end{aligned}$$

since the reference occupations $q^0 \in \{0, 1\}$.

If we rewrite Eq. (A1) as $\mathscr{N} = \operatorname{Tr}\mathbf{\Gamma}_\infty + \mathscr{R}(\boldsymbol{q}^0)$, we consider this as a partitioning of $\mathscr{N}$ in an atomic reference part and a residual molecular contribution. The same result can be obtained more systematically by a second order Taylor expansion of $\operatorname{Tr}\mathbf{\Gamma}$. This is demonstrated in Appendix B.

Appendix B: Taylor expansion

In this Appendix we demonstrate that the respective electron pair valence indices measure the sum of the first- and second-order changes, in the Taylor expansion sense (around the SAL reference), of the associated generating functions, which appear in the $\mathbf{\Gamma}$-matrix normalization equation. For example, in the UHF scheme:

$$\operatorname{Tr}\mathbf{\Gamma} = \sum_A [\Phi_A(n_A, \boldsymbol{q}_A) + \Omega_A(\boldsymbol{P}'_A)] + \sum_{a\neq}\sum_B [\Phi_{AB}(n_A, n_B) + \Omega_{AB}(\boldsymbol{P}_{AB})] \qquad \text{(B1)}$$

where Φ and Ω stand for the ionic and covalent generating functions; their explicit forms are:

$$\Phi_A = \tfrac{1}{2}\left\{n_A^2 - \sum_a^A [(q_a^\alpha)^2 + (q_a^\beta)^2]\right\} \qquad \text{(B2)}$$

$$\Phi_{AB} = n_A n_B \qquad \text{(B3)}$$

$$\Omega_A = V_A^{cov} \qquad \text{(B4)}$$

$$\Omega_{AB} = V_{AB}^{cov} \qquad \text{(B5)}$$

Here $\boldsymbol{P}'_A$ groups all off-diagonal elements of $\boldsymbol{P}_A$.

At the SAL reference state the following equations hold: $(n_A)_\infty = n_A^0$, $(\boldsymbol{q}_A)_\infty = \boldsymbol{q}^0$, $(\boldsymbol{P}'_A)_\infty = 0$ and $(\boldsymbol{P}_{AB})_\infty = 0$. Therefore the changes in the off-diagonal elements of the density matrix $\boldsymbol{P}$, relative to the SAL values are $\Delta\boldsymbol{P}'_A = \boldsymbol{P}'_A$ and $\Delta\boldsymbol{P}_{AB} = \boldsymbol{P}_{AB}$. It can be easily verified that the electron-pair valency numbers are the sums of the first- and second-order changes of the relevant generating functions in the following Taylor expansions:

$$\begin{aligned}\Delta\Phi_A &= \left(\frac{\partial\Phi_A}{\partial n_A}\right)_\infty \Delta n_A + \sum_a^A \left(\frac{\partial\Phi_A}{\partial q_a}\right)_\infty \Delta q_a \\ &\quad + \frac{1}{2}\left[\left(\frac{\partial^2\Phi_A}{\partial n_A^2}\right)_\infty \Delta n_A^2 + \sum_a^A \left(\frac{\partial\Phi_A}{\partial q_a^2}\right)_\infty \Delta q_a^2\right] = V_A^{ion} \qquad \text{(B6)}\end{aligned}$$

$$\Delta\Phi_{AB} = \left(\frac{\partial\Phi_{AB}}{\partial n_A}\right)_\infty \Delta n_A + \left(\frac{\partial\Phi_{AB}}{\partial n_B}\right)_\infty \Delta n_B + \left(\frac{\partial^2\Phi_{AB}}{\partial n_A\,\partial n_B}\right)_\infty \Delta n_A\,\Delta n_B = V_{AB}^{ion} \qquad \text{(B7)}$$

$$\Delta\Omega_A = \sum_{a<}^{A}\sum_{a'}^{A}\left[\left(\frac{\partial\Phi_A}{\partial P_{aa'}}\right)_{\infty}\Delta P_{aa'} + \frac{1}{2}\left(\frac{\partial^2\Omega_A}{\partial P^2_{aa'}}\right)_{\infty}\Delta P^2_{aa'}\right] = V_A^{cov} \tag{B8}$$

$$\Delta\Omega_{AB} = \sum_{a}^{A}\sum_{b}^{B}\left[\left(\frac{\partial\Omega_{AB}}{\partial P_{ab}}\right)_{\infty}\Delta P_{ab} + \frac{1}{2}\left(\frac{\partial^2\Omega_{AB}}{\partial P^2_{ab}}\right)_{\infty}\Delta P^2_{ab}\right] = V_{AB}^{ion} \tag{B9}$$

It should be observed that the first-order term of each covalent term expansion vanishes due to the assumed form of the density matrix in the SAL.

This Taylor expansion interpretation clearly demonstrates that the valence numbers in fact measure the changes of the generating pairing functions relative to the reference SAL values. Notice, that the covalent valence quantities are themselves the generating functions, thus exhibiting a special invariance property. The above analysis also emphasizes the difference character of the valence numbers, in accordance with intuitive classification of the valency itself as being an electron pairing difference phenomenon.

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