

# A definition for the covalent and ionic bond index in a molecule

## An approach based on Roby's atomic projection operators

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**Abstract** Formulae for hermitian operators representing covalent, ionic, and total bond indices are derived. The eigenstates of these operators come in pairs, and can be considered as bonding, anti-bonding and lone-pair orbitals. The form of these operators is derived by generalising the rule that the bond order be defined as the net number of bonding electron pairs. The percentage of covalency and ionicity of a chemical bond may be obtained, and bond indices can also be defined between groups of atoms. The calculation of the bond indices depends only on the electron density operator, and certain projection operators used to represent each atom in the molecule. Bond indices are presented for a series of first and second row hydrides and fluorides, hydrocarbons, a metal complex, a Diels–Alder reaction and a dissociative reaction. In general the agreement between the bond indices is in accord with chemical intuition. The bond indices are shown to be stable to basis set expansion.

**Keywords** Bond index · Bond order · Ionic bond index · Covalent bond index · Roby projection operator

### 1 Introduction

The role that quantum chemical calculations play in solving chemical problems can be summarised as follows.

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1. *High level formulation* The chemical problem is first defined in terms of high level concepts and language. For example, an organic chemist might ask: “How do I modify a particular molecule with substituents to favor a particular reaction?”.
2. *Quantum reformulation with simplifying hypotheses* The problem is then re-phrased in the language of quantum chemistry. Now the problem is invariably too complex to handle, so a range of hypotheses must be formulated about the properties which are relevant to the problem. For example, the organic chemist might postulate a number of possible candidate substituents, and then hypothesize that the predisposition of the substituted molecules to reaction is closely correlated to energy differences associated with the detailed stereoscopic arrangement of a limited number of the atoms in the molecule.
3. *Quantum chemical calculations* Finally, in the end-game, quantum chemical calculations are performed on a list of candidate geometric structures. The solution to the original problem is then selected as the best choice from this reduced list of possibilities.

Computer calculation methods in quantum chemistry pioneered by John Pople and others [1] are now highly developed, so the end-game is less an obstacle than it once was. On the other hand, techniques which help in the formulation of the initial problem and which help in formulating the hypotheses which reduce the problem complexity are less well developed.

To be specific: how does the organic chemist choose the substituents and geometric structures to be submitted for quantum mechanical calculation? Obviously these decisions are not made in vacuo. Instead, there is a body of very important “higher level” knowledge which is drawn upon both to phrase the initial hypothesis, and to limit the possibilities that

should be investigated. All this is done *before* the quantum mechanical calculations are performed.

These “higher level” or “valence” concepts we allude to are those that are central to chemistry. For example, the concept of a molecule composed of “atoms” with certain properties quite different to those of the isolated atom. Or, the concept of a “bond” between atoms in a molecule, often drawn as lines between the atoms, and which is used to classify the strength of the interactions between atoms. The “bond order” allows intuitive guesses to be made about the kind of reactions that the bonded atom might be involved in, and it allows a prediction of the number and type of atoms that might be found as neighbours.

Chemists have noticed empirically that atoms or groups of atoms which have a common geometric motif and bonding pattern often behave collectively in more-or-less the same manner. They have rationalized the properties of these “functional groups” of atoms in terms of other higher level concepts such as “charge”, “reactivity”, “electronegativity”, “hardness”, or “softness”, and simple rules or theories have been proposed that explain the relationships expected between these concepts. These are very useful concepts which greatly aid in thinking about complex chemical problems, help in reducing their complexity, and help in predicting chemical behaviour. Because of their utility, these concepts persist today, despite the fact that there is no natural definition for them within quantum theory.

It is the purpose of this paper to make a link between quantum chemistry and traditional notions of a chemical bond. Specifically, we furnish here a rigorous definition of what is meant by a chemical bond within quantum mechanics. In this way, the process by which chemical problems are solved and formulated will be enhanced, since the quantum chemical calculations would provide not only numerical results, but also qualitative bonding information important in obtaining insight and understanding in terms of broader chemical concepts whose utility is well established.

### 1.1 New definitions for the covalent and ionic bond order

According to Pauling [2], a bond between two atoms may be said to have a certain amount of covalency or ionicity [2]. The covalency and ionicity of a bond are very useful qualitative concepts for chemists, and Pauling was the first to give a quantitative measure of these concepts based on the electronegativity differences of the atoms involved in the bond.

In this paper we present a new definition of bond order, which we call the *bond index*. The bond index is defined in terms of two other indices: the *covalent bond index* and the *ionic bond index*. These two indices are defined in the usual way for quantum mechanical observables, as the expectation value of two different hermitian operators. Together, these bond indices yield an estimation of the percentage of

covalency and ionicity of a bond which can be calculated from any quantum mechanical wavefunction.

Our development of the bond index formula builds upon Roby’s projection operator theory [3–6], which was based on ideas originally proposed by Davidson [7], and has since been developed also by others [8–10]. In Roby’s theory, an atom  $A$  is represented by a projection operator  $P_A$  in a Hilbert space, while a group of atoms  $A \dots B$  is represented by a projection operator  $P_{A\dots B}$ . These projection operators admit a rigorous and elegant definition of atomic populations, group populations, populations “shared” and “transferred” between atoms, and between groups of atoms. The sharing of electronic population between a pair of atoms is the essence of covalency, whilst the transfer of population is the essence of ionicity. The definition of shared and transferred populations leads naturally to definitions of the Roby (or “covalent”) operator  $\mathcal{R}$ , and a corresponding “ionic” operator  $\mathcal{I}$ ,

$$\mathcal{R} = P_A + P_B - P_{AB}, \quad (1)$$

$$\mathcal{I} = P_A - P_B. \quad (2)$$

When these operators are “normalised”, we obtain the ionic and covalent bond index operators, whose expectation value is used to calculate the ionic and covalent bond indices between two atoms, respectively

$$\hat{c}_{AB} = \frac{\mathcal{R}}{2|\mathcal{R}|}, \quad (3)$$

$$\hat{i}_{AB} = \frac{\mathcal{I}}{2|\mathcal{I}|}. \quad (4)$$

(The absolute value of an operator, say  $|\mathcal{R}|$ , is defined by the fact that it has the same eigenstates as the operator  $\mathcal{R}$ , but the corresponding eigenvalues of these eigenstates are the absolute values of those for  $\mathcal{R}$ ).

It is worth emphasizing the key features of the bond indices introduced in this paper that set it apart from the many other definitions of bond indices:

- The formulae for the bond indices depend only on the one-electron reduced density *matrix* and certain *hermitian* projection operators which define the atoms; hence the formulae can be applied to any type of *ab initio* wavefunction, and are independent of the basis set used to expand the wavefunction.
- Upon increasing the basis set size used to expand the wavefunction, the bond indices converge smoothly to a limit.
- When appropriate covalent and ionic bonding and antibonding orbitals are defined, as eigenstates of the covalent and ionic operators, the covalent and ionic bond indices can be derived according to the usual rule for a bond index in a homonuclear diatomic molecule, as half the difference between the number of electrons in the bonding

and anti-bonding orbitals i.e., the net number of bonding electron pairs.

- Together with the total bond index, the covalent and ionic bond indices allow the percentage of covalent and ionic character of a bond to be calculated.
- The ionic bond index is defined on equal terms with the covalent bond index.

## 1.2 Continuing interest in bond orders

Several examples are now discussed to show that the bond order concept continues to play an important role in theoretical and experimental sciences. We also mention how our work impacts on these examples.

- In 1997, Robinson et al. [11] reported the synthesis of a compound which was claimed to have the first example of a Ga–Ga triple bond. Shortly afterwards, another compound was described by the same group having the shortest Fe–Ga bond on record, also claimed to be a triple bond [12]. Controversy surrounded these publications concerning whether the bonds concerned were actually triple bonds, and the papers spawned further theoretical and experimental studies [13]. The arguments and controversy surrounding the existence of these triple bonds is, in our opinion, not as important as the fact that the bond index was used as a marker to recognise a new and unusual kind of chemical compound. More recently, in 2005, Nguyen et al. [14] reported the synthesis of a new compound displaying a Cr–Cr quintuple bond [15]. Attempts to formalise a definition of bond order, as in this paper, are relevant to these synthetic and theoretical attempts to clarify the notion of bonding in unusual compounds.
- Bond orders are routinely obtained from electron densities measured by X-ray diffraction experiments [16]. Here, the bond order is not the number of electron pairs associated with the atom–atom interaction, but it is the value of the electron density at the bond critical point on the topological “bond path” connecting the bonded atoms [16]. The bond index formula we propose in this paper requires the electron density *matrix*, but such density matrices can nevertheless also be obtained from accurate X-ray experiments [17,18]. Thus the bond index formula we present here could also be derived from experiment.
- Physicists have realised that quantum mechanical calculations do not offer by themselves a sufficiently simple and informative model to understand solid state structure. The electron localisation function (ELF) has been introduced with some success in these explanatory efforts [19]. The topological attractor basins of the ELF have been found to be correlated with classical notions of

chemical bonding i.e., number of bonds, lone pairs, and so on [20]. Our work provides an alternative to this ELF-based approach.

## 1.3 Outline of the paper

There is, of course, a very large literature on the subject of bond indices derived from quantum mechanics—a fact which further highlights the interest in the bond index concept, and indicates the variety of opinions and approaches which exist. Only a brief summary is given here, in the following section; for more details we refer to the extensive review of the bond order literature prior to 1992, by Sannigrahi [21].

The bulk of this paper is devoted to the derivation of the bond index formula. For the most part, mathematical theorems are proved and used. The physical content of our formulae can be traced to two main sources:

1. In the arguments which motivation the choice of the operators themselves.
2. In the definition of the atomic projectors which define the atoms.

Illustrative calculations are presented for the bond indices in a range of molecules, including the bond indices during reaction and bond-breaking processes. Some deviations from chemical expectations are noted and discussed, and our conclusions are given in the final section.

## 2 Bond indices from quantum mechanics: a brief review

The origins of the bond index concept date back to simple MO theory. There, the *bond order* is defined as half of the difference between the number of electrons in bonding orbitals and the number of electrons in anti-bonding orbitals. However, such a definition can only be applied to diatomics. Coulson [22] was the first to provide a definition that could be applied to polyatomic molecules. Not long after, Chirgwin [23], McWeeny [24,25], and Mulliken [26,27], among others, contributed further definitions. All these definitions depend linearly on elements of the first order density matrix, as does our definition. Wiberg [28], on the other hand, introduced a bond order definition that depends quadratically on the density matrix, and also called it a bond index. (Other names for bond index that have appeared in the literature include: bond valency, bond order index, and degree of bonding).

Mayer [29] was the first to initiate the ab initio calculations of bond indices (in contrast to the semi-empirical calculations done earlier) using definitions based on Mulliken’s population analysis. Other ab initio bond order definitions are based on Löwdin’s population analysis [30]. A common

feature of these definitions is that they were developed for single determinant HF calculations. However, the same formulas are commonly used for correlated wavefunctions, once the first order density matrix is extracted (for an exception see [31]).

Sannigrahi [21] notes that the indices introduced by the afore-mentioned researchers measured the number of electrons on atom *A* covalently bonded to those on atom *B*. However, he states that “Deviations from classical integral values are ascribed to the ionic character of the bonds.” Thus a crude measure of the covalency or ionicity of bond could be obtained.

Another operationally complicated but popular definition of bond order is due to Weinhold and coworkers [32], who have extensively developed the early ideas of atomic hybridisation into the “natural bond orbital” method. The natural atomic and bond orbitals of this method are localised over one and two atomic centres, respectively, thus facilitating descriptions of the molecule in terms of valence concepts such as atomic charge, bond order and valence.

Cioslowski and Mixon [33,34] have extended Bader and coworkers theory of atoms in molecules (AIM) [35] to define “covalent” bond orders for bonds connecting “atomic basins”. Additionally, they defined the degree of ionicity of a bond in terms of relative population differences between the pair of atoms that form the bond. Cioslowski and Mixon’s definition of bond order is given in terms of localised orbitals and the AIM partitioning of space, and therefore its “form” is not strictly invariant to a unitary transformation; Ángyán et al. [36] extended the definition so that it was. Raub and Jansen [37] have proposed to derive an indication of bond polarity by combining the use of the AIM atomic basins with those of the ELF.

Fulton [38] has described the use of sharing indices based on the density matrix amplitude. Bond orders are shown to be twice these sharing indices, and they have been compared to the method of Cioslowski and Mixon, mentioned above [39]. The sharing indices are found to be similar to the covalent bond orders of Cioslowski and Mixon, and do not display some pathological behaviour for the bonds in benzene.

Yamasaki et al. [40] have introduced the correlation analysis of chemical bonds (CACB) method which uses a hierarchy of operators to extract chemical valence properties from molecular wave functions. These operators include a non-hermitian bond order operator, whose expectation gives the same formula as obtained by Mayer and others in their statistical interpretation of bond order.

To summarise, it appears that the concept of an ionic bond index has not yet been separately defined anywhere in the literature, on an equal footing with the covalent bond index. Neither have hermitian operators been associated with these bond indices. Nor have bond indices been defined between functional groups of atoms.

### 3 Covalent, ionic, and total bond indices

In order to motivate the definition of the covalent, ionic, and total bond indices, it is necessary to first review the basic concepts of Roby’s population analysis scheme. Another key step is the introduction of a new definition of the ionic transfer population, which complements Roby’s original definition of shared population. Both the shared population and the ionic transfer population are the expectation value of two operators, the Roby and ionic operators, respectively. We demonstrate that the Roby and ionic operators are connected by an interesting pythagorean relationship. Furthermore, their eigenstates occur in pairs, and the corresponding eigenvalues maximise or minimise the shared and ionic transfer populations: effectively the Roby and ionic operators define bonding and antibonding orbital pairs which we argue are appropriate for the description of covalent and ionic bonding. The formula for the bond indices then follows by applying the usual rule for bond order, as half the difference in the populations of the bonding and antibonding orbitals.

#### 3.1 Atoms, atomic projection operators and populations

One of Roby’s central ideas is that the electrons in an atom should be represented by a set of one-electron basis functions. More specifically, it is the vector space  $V_A$  represented by the span of these basis functions which is defined to be the atom, which we hereafter refer to as the Roby atom. Then, given a reduced one-particle density operator

$$\rho = \sum_{ij} |\eta_i\rangle \lambda_i \langle \eta_j|, \quad (5)$$

defined in terms of natural orbitals  $|\eta_i\rangle$  and occupation numbers  $\lambda_i$ , the population  $n_A$  associated with a subspace  $V_A$  is given by

$$n_A = \langle P_A \rangle \equiv \text{Tr}(\rho P_A), \quad (6)$$

where  $P_A$  is the projector onto the basis functions of subspace  $V_A$ . If  $\{|i\rangle\}$  is a basis for the subspace  $V_A$ , then it is easily verified that the projection operator  $P_A$  onto  $V_A$  is given explicitly by [41]

$$P_A = \sum_{ij \in A} |i\rangle S_{ij}^{-1} \langle j|, \quad (7)$$

where  $S_{ij}^{-1}$  is an element of the inverse of the overlap matrix between elements of the basis set,

$$S_{ij} = \langle i|j\rangle. \quad (8)$$

It is important to note two points. First, while the details of choosing the basis functions for space  $V_A$  are crucial from a physical point of view, the selection of these basis functions

is not important for the definition of the bond index formulas presented below. We will specify in detail our particular choice later: essentially they will be the occupied natural orbitals associated with the atom centered at the position of atom  $A$ . Second, a Roby atom may be comprised of a number of different physical atoms. For example, if the Roby atom was comprised of the atom pair  $A$  and  $B$ , the population of this atom pair would be given by

$$n_{AB} = \langle P_{AB} \rangle, \quad (9)$$

where  $P_{AB}$  is the projection operator for the subspace  $V_{AB} = V_A + V_B$ , the subscript “ $AB$ ” being used to denote “sum of spaces  $A$  and  $B$ ”.

### 3.2 Shared and ionic populations

It is important to keep in mind that the Roby atoms of a molecule in general *overlap*. The consequence of this is that the sum of the populations on each atom in the molecule, as calculated by Eq. (6), is not equal to the total number of electrons in the molecule. Thus, for a pair of atoms  $A$  and  $B$ ,  $n_{AB}$  as defined by (9) does not necessarily equal  $n_A + n_B$ . The difference between  $n_{AB}$  and  $n_A + n_B$  is a measure of the electronic population that is shared between the atoms  $A$  and  $B$ . Thus Roby defined the shared population as

$$s_{AB} = n_A + n_B - n_{AB}, \quad (10)$$

which can be written as

$$s_{AB} = \langle \mathcal{R} \rangle, \quad (11)$$

where  $\mathcal{R}$  is the Roby (or “covalent”) operator already defined at the start of the paper (equation (77) in reference [4]),

$$\mathcal{R} = P_A + P_B - P_{AB}. \quad (12)$$

The amount of electron sharing between a pair of atoms is intuitively related to the bond strength and “covalency” between these atoms. Consequently, the Roby operator (12), whose expectation gives a measure of electron sharing, can be naturally associated with the concept bond strength, and in particular covalency.

Complementing the concepts of electron sharing and covalency are the concepts of charge transfer and ionicity. For a particular pair of atoms  $A$  and  $B$  in a molecule, the amount of charge transfer between the pair is related to the difference in the populations on those atoms minus their atomic charge, that is,

$$i_{AB} = n_A - n_B + Z_B - Z_A = \langle \mathcal{I} \rangle + Z_B - Z_A. \quad (13)$$

We shall refer to  $i_{AB}$  as the “ionic transfer population”. The Ionic operator was already defined at the start of the paper as

$$\mathcal{I} = P_A - P_B. \quad (14)$$

The following subsections demonstrate that the properties of  $\mathcal{R}$  and  $\mathcal{I}$  defined in this way are most useful for developing ideas of covalent and ionic bonding.

Our principal focus in this paper is the bond between atoms  $A$  and  $B$ . Since the operators  $\mathcal{R}$  and  $\mathcal{I}$  only involve the spaces  $V_A$  and  $V_B$  associated with the bond between atoms  $A$  and  $B$ , we therefore restrict our discussion to the space  $V_A + V_B$  in the rest of the paper. With this restriction, the projection operator  $P_{AB}$  becomes the identity operator i.e.,  $P_{AB} = 1$  in Eq. (12).

### 3.3 Pythagorean relationship between the Roby and Ionic operators relation

Using the basic properties of projection operators (e.g.,  $P_A^2 = P_A$  and  $P_A P_{AB} = P_{AB} P_A = P_A$ ) it is easy to show that the Roby and ionic operators obey the pythagorean relation

$$\mathcal{R}^2 + \mathcal{I}^2 = 1. \quad (15)$$

The pythagorean relation is important because it provides a formal link for the intuitive notion that the concepts of population sharing and population transfer are in some sense related and complementary. With this in mind, we will continue with a description of the properties of the operators  $\mathcal{R}$  and  $\mathcal{I}$ , and  $\mathcal{R}^2$  and  $\mathcal{I}^2$ .

### 3.4 Commutation properties of the Roby and Ionic operators: paired eigenspaces

Even though both the Roby operator  $\mathcal{R}$  and the ionic operator  $\mathcal{I}$ , are constructed from projection operators, they are not themselves projection operators. Neither do these operators commute; in fact, it is easy to show that  $\mathcal{R}$  and  $\mathcal{I}$  anticommute. In appendix A it is shown that this implies that the eigenstates of  $\mathcal{R}$  and  $\mathcal{I}$  come in *pairs* whose eigenvalues have opposite sign.

Despite the fact that  $\mathcal{R}$  and  $\mathcal{I}$  do not commute, it is straightforward to show that  $\mathcal{R}^2$  and  $\mathcal{I}^2$  commute with both  $P_A$  and  $P_B$ , and hence also with each other. A consequence of the fact that  $\mathcal{R}^2$  and  $\mathcal{I}^2$  commute is that they may share a common set of eigenstates.

### 3.5 Angles for labelling the paired eigenspaces of the Roby and Ionic operators

Since  $\mathcal{R}^2$  and  $\mathcal{I}^2$  share a common set of eigenstates, according to the pythagorean relation, their eigenvalues for a particular simultaneous eigenstate sum to one. In appendix B a stronger result is demonstrated: namely, that the eigenvalues of  $\mathcal{R}^2$  and  $\mathcal{I}^2$  lie between zero and one. It is therefore possible to assign an “angle”  $\theta$  to the simultaneous eigenstates of  $\mathcal{R}^2$  and  $\mathcal{I}^2$ , such that for a given simultaneous eigenstate

$|\theta\rangle$  the eigenvalue of  $\mathcal{R}^2$  is  $\cos^2 \theta$  while the eigenvalue of  $\mathcal{S}^2$  is  $\sin^2 \theta$ ,

$$\mathcal{R}^2|\theta\rangle = \cos^2 \theta|\theta\rangle, \quad (16)$$

$$\mathcal{S}^2|\theta\rangle = \sin^2 \theta|\theta\rangle \quad (17)$$

In fact, the Roby and ionic operators are closely related to Araki's angle operators [42], which generalise the notion of an angle between two lines (i.e., two monodimensional vector spaces) to angles between multidimensional spaces. According to Araki, the cosine of the "angles"  $\theta$  between two vector spaces  $V_A$  and  $V_B$  are given by the absolute value of the eigenvalues of  $\mathcal{R}$ ; likewise, the sine of the "angles" between the two spaces are given by the absolute value of the eigenvalues of  $\mathcal{S}$ . Since the eigenstates of the Roby and ionic operators come in pairs whose eigenvalues have opposite sign, Araki's result allows us to write

$$\mathcal{R}|\pm \cos \theta\rangle = \pm \cos \theta|\cos \theta\rangle, \quad (18)$$

$$\mathcal{S}|\pm \sin \theta\rangle = \pm \sin \theta|\sin \theta\rangle. \quad (19)$$

The eigenstates have been labelled by their corresponding eigenvalues.

In Appendix C, we prove the equations above and we further demonstrate the important fact that the pair of eigenstates with non-zero eigenvalues,  $\{|\pm \cos \theta\rangle\}$  and  $\{|\pm \sin \theta\rangle\}$ , span the same subspace. We call this subspace  $V_\theta$ , Araki's  $\theta$ -angle eigenspace. Araki's angle provides a convenient labelling for these eigenspaces. The bond index formula we will develop later will be expressed initially in terms of these important paired eigenspaces.

### 3.6 Properties of the paired eigenstates of the Roby and Ionic operators: maximum overlap and extreme population

The Roby and ionic operators have two properties which link them to qualitative ideas of bonding. These properties are related to their eigenstates, their associated populations, and the pairing theorem.

First, consider the pairing theorem and its relevance. According to the pairing theorem [43] (see also [44]) given two orthonormalised sets,  $\{|a_i\rangle\}$  and  $\{|b_j\rangle\}$  which respectively span the spaces  $V_A$  and  $V_B$ , there exist unitary transformations giving orthonormalised sets,  $\{|a'_i\rangle\}$  and  $\{|b'_j\rangle\}$ , such that the overlap matrix  $\langle a'_i|b'_j\rangle$  is diagonal in  $i$  and  $j$ . Further, the new basis function pairs  $\{|a'_i\rangle, |b'_i\rangle\}$  are those that extremise their overlap  $\langle a'_i|b'_i\rangle$  with each other [4] (see also Appendix C). The concept of maximum overlap plays an important role in many theories of bond formation [45].

The importance of the pairing theorem in relation to the Roby and ionic operators rests on the following two properties, proved in appendices C and D:

1. The paired eigenstates of  $\mathcal{R}$  and  $\mathcal{S}$  with non-zero eigenvalue, respectively,  $\{|\pm \cos \theta\rangle\}$  and  $\{|\pm \sin \theta\rangle\}$ , are linear combinations of *only two* of the maximally overlapping basis functions e.g.,  $|a'_i\rangle$  and  $|b'_i\rangle$ . This strongly suggests that the paired eigenspaces  $V_\theta$  of  $\mathcal{R}$  and  $\mathcal{S}$  could be used to develop ideas of chemical bonding.
2. The paired eigenstates of  $\mathcal{R}$  (and respectively,  $\mathcal{S}$ ) have extreme values (either maxima or minima) of the shared population  $s_{AB}$  (or respectively, the ionic transfer population  $i_{AB}$ ) when restricted to the paired space  $V_\theta$ . Consequently the paired eigenstates of  $\mathcal{R}$  (respectively  $\mathcal{S}$ ) can be regarded as bonding and antibonding orbitals for shared populations (respectively, the ionic transfer population) within  $V_\theta$ . This strongly suggests using the eigenstates of  $\mathcal{R}$  and  $\mathcal{S}$  to define bond indices associated with electron sharing, and ionic transfer.

In a later subsection we use these two key properties to motivate the development of the bond index formulas.

### 3.7 Meaning of the zero-eigenvalue eigenstates of the Roby and Ionic operators: linear dependence and non-bonding orbital

The discussion above has concentrated on the pairing of *non-zero* eigenvalues of the Roby and ionic operators. Here we demonstrate that the zero-eigenvalues of the Roby and ionic operators also have a useful meaning.

The zero-eigenvalue eigenstates of the ionic operator belonging to the space  $V_{\theta=0}$  satisfy  $\mathcal{S}|\lambda\rangle = (P_A - P_B)|\lambda\rangle = 0$  (since  $\sin 0 = 0$ ). It can be shown that in this case we must have  $|\lambda\rangle \in V_A \cap V_B$ . That is, the zero-eigenvalue eigenstates of  $\mathcal{S}$  correspond to functions which are linearly dependent.

On the other hand the zero eigenvalue eigenstates of the Roby operator belonging to the space  $V_{\theta=\pi/2}$  satisfy  $\mathcal{R}|\lambda\rangle = 0$  or  $(P_A + P_B)|\lambda\rangle = P_{AB}|\lambda\rangle$  (since  $\cos \pi/2 = 0$ ). In this case, it can be shown that the eigenstates are comprised of the functions in  $V_A$  orthogonal to  $V_B$  and those in  $V_B$  orthogonal to  $V_A$  i.e.,  $|\lambda\rangle \in V_A \cap \bar{V}_B \oplus V_B \cap \bar{V}_A$ . A physical notion of what this space means can be given. Assuming that the spaces  $V_A$  and  $V_B$  are defined by atomic natural orbitals on each atom (see Sect. 3.14 later) we expect that the core natural orbitals on one atom overlap only weakly with orbitals on the other atom. Hence these core orbitals can be said to (roughly speaking) belong to the zero-eigenvalue subspace of the Roby operator,  $V_{\theta=\pi/2}$  subspace. Likewise, very diffuse orbitals on one atom such as valence lone pair orbitals (constructed as a linear combination of the atomic valence natural orbitals) would also overlap very weakly with the atomic orbitals on the other atom, and would also belong to  $V_{\theta=\pi/2}$ . In short, the eigenstates of  $V_{\theta=\pi/2}$  are comprised of "non-bonding" orbitals.

### 3.8 The covalent and ionic bond index formula

According to the simple MO theory of homonuclear diatomic molecules, the bond order is defined as half the difference in the number of electrons in the bonding and antibonding orbitals. At the same time, we have seen that the eigenstates of the Roby and ionic operators,  $\mathcal{R}$  and  $\mathcal{I}$ , occur in bonding and antibonding pairs. The populations of each of these bonding or antibonding orbitals may be calculated according to Eq. (6), where  $P_A$  is chosen to be the projector onto the appropriate bonding or antibonding eigenstate. Thus, we can combine the bond order rule with the bonding and antibonding orbitals of the Roby operator to obtain a covalent bond index. Likewise, we can combine the populations of the ionic bonding and antibonding orbitals to obtain the ionic bond index.

These considerations can be made more explicit. Specifically, we define

$$n_c^\pm = \left\langle P_{c,\theta}^\pm \right\rangle, \quad (20)$$

$$n_i^\pm = \left\langle P_{i,\theta}^\pm \right\rangle, \quad (21)$$

where  $n_c^\pm$  are the populations of the covalent bonding and antibonding eigenstates  $|\pm \cos \theta\rangle$ ,  $n_i^\pm$  are the populations for the ionic bonding and antibonding eigenstates  $|\pm \sin \theta\rangle$ , (the + sign indicates the bonding eigenstate and the—sign indicates the antibonding eigenstate), and where the covalent and ionic projection operators are, respectively,

$$P_{c,\theta}^\pm = |\pm \cos \theta\rangle\langle \pm \cos \theta|, \quad (22)$$

$$P_{i,\theta}^\pm = |\pm \sin \theta\rangle\langle \pm \sin \theta|. \quad (23)$$

Then the covalent and ionic bond indices for the paired states with angle  $\theta$  are defined respectively by

$$c_\theta = (n_c^+ - n_c^-)/2, \quad (24)$$

$$i_\theta = (n_i^+ - n_i^-)/2. \quad (25)$$

According to the previous discussion,  $n_c^+$  and  $n_c^-$  are the maximum and minimum shared populations (respectively) that can be obtained within the bonding eigenspace  $V_\theta$ . Likewise  $n_i^+$  and  $n_i^-$  are the maximum and minimum ionic transfer populations that can be obtained in the same subspace. The covalent and ionic bond indices are then obtained by summing over all paired eigenspaces with nonzero eigenvalues  $\cos^2 \theta$ ,

$$c_{AB} = \sum_{\theta < \pi/2} c_\theta, \quad (26)$$

$$i_{AB} = \sum_{\theta > 0} i_\theta. \quad (27)$$

It should be noted that both the covalent and ionic bond indices can be negative. A negative value for the ionic bond index only indicates that there is a net excess of electrons on atom

$B$  in a bond in  $AB$ . However, a negative value for the covalent bond index in general indicates a true anti-bonding orbital.

As mention in Sect. 3.7, the eigenspaces where the Araki angle  $\theta = \pi/2$ ,  $V_{\theta=\pi/2}$  contains non-bonding orbitals. Such orbitals are not appropriate for describing covalent bonding interactions, and so should not be included in the summation to for the total bond index vector; hence the restriction to angles strictly less than  $\pi/2$  in the formula (26). Alternatively, we can extend the summation over all angles with the understanding that  $c_{\theta=\pi/2} = 0$ . Likewise, the space  $V_{\theta=0}$  which arises due to linear dependencies between the atomic natural orbital spaces of atoms  $A$  and  $B$  offers no possibility of population transfer from one atom to another, so it is appropriate that no ionic bond index should be defined on such spaces (such spaces may, however, contribute to the covalent bond index). Hence the restriction to angles strictly greater than in the formula (27); or alternatively, the summation may be unrestricted with the understanding that  $i_{\theta=0} = 0$ .

### 3.9 The covalent and ionic bond index operators

The formula for the covalent and ionic bond indices can be recast in a more elegant form. Consider the operator  $\mathcal{R}/2|\mathcal{R}|$ , which has the same eigenstates as  $\mathcal{R}$  except that the non-zero eigenvalues corresponding to the bonding orbitals are  $1/2$  while those for the antibonding orbitals are  $-1/2$ . That is,

$$\frac{\mathcal{R}}{2|\mathcal{R}|} = \frac{1}{2} \sum_{\theta < \pi/2} (|\cos \theta\rangle\langle \cos \theta| - |-\cos \theta\rangle\langle -\cos \theta|). \quad (28)$$

Using this definition, it can be seen that the expectation value of this operator yields the bond index for the covalently shared electrons,

$$c_{AB} = \left\langle \frac{\mathcal{R}}{2|\mathcal{R}|} \right\rangle. \quad (29)$$

i.e., this expectation value gives half the population of electrons in the bonding covalent orbital minus the antibonding covalent orbital. The formula for the ionic bond index follows the same line of reasoning: writing the spectral decomposition

$$\frac{\mathcal{I}}{2|\mathcal{I}|} = \frac{1}{2} \sum_{\theta > 0} (|\sin \theta\rangle\langle \sin \theta| - |-\sin \theta\rangle\langle -\sin \theta|) \quad (30)$$

the ionic bond index is given by

$$i_{AB} = \left\langle \frac{\mathcal{I}}{2|\mathcal{I}|} \right\rangle \quad (31)$$

The operators  $\hat{c}_{AB} = \mathcal{R}/2|\mathcal{R}|$  and  $\hat{i}_{AB} = \mathcal{I}/2|\mathcal{I}|$  are, respectively, the covalent and ionic bond index operators. We have thus recast the bond index formula in terms of the expectation value of two hermitian operators. We note that the rules of quantum mechanics require that observables be represented by hermitian operators.

### 3.10 The hybrid spin

We have spent some time on the properties of the  $\mathcal{R}$  and  $\mathcal{S}$  operators. However, the operators  $\hat{c}_{AB}$  and  $\hat{i}_{AB}$  just defined are also connected by a relationship, which is used in the derivation of the formula for the total bond index. If we define

$$s_x = \hat{c}_{AB}, \quad (32)$$

$$s_z = \hat{i}_{AB}, \quad (33)$$

and make the additional definition

$$s_y = \frac{i[P_A, P_B]}{2|\mathcal{R}||\mathcal{S}|}, \quad (34)$$

(note that  $i$  in the equation above refers to the  $\sqrt{-1}$ ) then it can be shown that

$$s_x^2 = s_y^2 = s_z^2 = 1/4 \quad (35)$$

and also

$$[s_x, s_y] = is_z, \quad [s_y, s_z] = is_x, \quad [s_z, s_x] = is_y \quad (36)$$

That is, the three operators  $s_x$ ,  $s_y$  and  $s_z$  obey the same commutation relations as the components of the spin operator i.e., they obey an  $SU(2)$  commutation law. (To see that this is true consider the representation of  $\hat{c}_{AB}$  and  $\hat{i}_{AB}$  in the basis  $\{|\pm \sin \theta\rangle\}$ —see appendix C, Eq. (64)—and then define  $s_y$  by the last equation above). We therefore call the operator  $s$  the hybrid spin operator.

### 3.11 The bond index formula

We have seen that the paired eigenspaces of the Roby and ionic operator admit an elegant definition of the covalent and ionic bond index. The paired spaces contain orbitals which have extremes of shared population and ionically transferred population. It seems reasonable that this paired space should form the basis of a definition of a bond index, one that includes both the contributions from covalent and ionic parts. To motivate a bond index formula, we therefore consider the eigenstates which have extreme population  $\langle P_{AB} \rangle$  within this paired eigenspace. Appendix E shows that these eigenstates may be easily calculated. If we again use the simple bond order rule, we may derive a total bond index for the paired eigenspace. The final result is

$$\tau_\theta = \sqrt{c_\theta^2 + i_\theta^2} \quad (37)$$

We then define a (total) bond index vector for the subspace  $V_{AB}$  by

$$\tau_{AB} = \sum_\theta (c_\theta, i_\theta). \quad (38)$$

(As will be explained later, for numerical reasons  $i_\theta$  is set to zero for angles  $\theta > \pi/2 - \epsilon$ , where  $\epsilon$  is a parameter). The

magnitude of this bond index vector defines the bond index for the bond between atoms  $A$  and  $B$ ,

$$\tau_{AB} = \|\tau_{AB}\| = \sqrt{c_{AB}^2 + i_{AB}^2}, \quad (39)$$

The bond index  $\tau_{AB}$  of a bond essentially gives the traditional bond order of the bond, which, as we will see later, gives values in very good agreement with traditional chemical intuitions. Note that the bond index is always a *positive* quantity, regardless of the sign of the covalent and ionic bond indices. The overall bonding or antibonding nature of the bond must be decided based on the sign of the covalent bond index.

### 3.12 The percentage of covalency and ionicity of a bond

The covalent  $c_{AB}$  and ionic  $i_{AB}$  bond indices just defined give an indication of how covalent or ionic a bond is. However, it seems conceptually simpler to refer to the (total) bond index (39) of the bond together with the percentage of covalency and/or ionicity of the bond. With this in mind, the percentage covalency and ionicity of a bond is defined as

$$\% \text{ Covalency} = 100 c_{AB}^2 / \tau_{AB}^2 \quad (40)$$

$$\% \text{ Ionicity} = 100 i_{AB}^2 / \tau_{AB}^2. \quad (41)$$

### 3.13 Circumventing problems with the ionic indices for non-diatomics

In practice, no problems are observed when calculating covalent bond indices for  $\theta$  close to  $\theta = \pi/2$  and  $\theta = 0$ , and no problems are observed for calculating ionic bond indices for spaces  $V_\theta$  close to  $\theta = 0$ . However, problems do arise when calculating ionic bond indices for values of  $\theta$  close to  $\pi/2$ . These problems originate in non-diatomic systems where at least one of the atoms  $A$  or  $B$  in the pair is in close proximity to other atoms, so that charge from these nearby atoms accumulates in the lone electron pair regions. The result is a distortion in the charge difference from what might be expected only from the atom pair  $AB$ . To avoid these problems, which in practice occur only when there are orbitals in angle spaces with angles close to  $\pi/2$ , we introduce a parameter  $\epsilon$  and set to zero those  $i_\theta$  where  $\theta > \pi/2 - \epsilon$ . In this work, the parameter is chosen so that  $\cos \epsilon = 0.025$ , which corresponds to an angle of about  $77^\circ$ . Thus, if  $\theta > 77^\circ$  then  $i_\theta = 0$ .

### 3.14 Explicit definition of the Roby atom

The definition of the atom used in this paper is that defined by way of the projection

$$P_W = \sum_{ij} |\eta_i^W\rangle S_{ij}^{-1} \langle \eta_j^W|, \quad (42)$$

where

$$S_{ij} = \langle \eta_i^W | \eta_j^W \rangle, \quad (43)$$

and where  $|\eta_i^W\rangle$  are the natural orbitals of the atom.

At this point, it needs to be noted that the projector can be defined for a grouping of atoms by defining the space of the projector to be that spanned by the occupied natural orbitals of each of the atoms at their respective positions in space (like a pro-molecule). In this case the natural orbitals between the atoms on different centers will not necessarily be orthogonal, and thus the overlap term of in the above expression must be retained. Whether the Roby atom is a single atom or a group of atoms is not important to the generalized theory outlined in the previous sections.

The definition (42) depends crucially on the natural orbitals included in the summation of this projection formula. The natural orbitals we use are defined in the following way:

1. The one-electron reduced density matrix  $\rho$  is obtained from the atomic wavefunction  $\Psi_A$ . In this paper, the Hartree–Fock approximation is used to obtain the atomic wavefunction.
2. The density matrix  $\rho$  is spherically averaged to form  $\bar{\rho}$  [46]. So, for example, Boron in the  $1s^2 2s^2 2p_x^1$  state becomes, loosely speaking,  $1s^2 2s^2 2p_x^{1/3} p_y^{1/3} p_z^{1/3}$ . The reason for this is that any assigned direction such as  $p_x$  would imply an arbitrary selection of a particular degenerate component of an atomic wavefunction  $\Psi_A$ , and the degeneracy of the  $p$ -orbitals implies that there should be no preference for any particular degenerate component.
3. Natural orbitals  $\eta_i^A$  are constructed from this spherical density  $\bar{\rho}$ ,

$$\bar{\rho} |\eta_i^A\rangle = n_i^A |\eta_i^A\rangle. \quad (44)$$

4. The atomic natural orbitals  $|\eta_i^A\rangle$  used to define the atomic projector are those which have an occupation  $n_i^A$  greater than 0.05 electrons.

The cut-off of 0.05 is used because orbitals with small occupation (and presumably with higher energy in the ground state) are not useful in the description of atomic properties and by increasing the size of the basis set the projectors will eventually span the whole space of the molecule. The cut-off value was chosen so that it would include the 1/3 occupations of the averaged  $p$ -orbitals, the 1/5 occupations of the  $d$ -orbitals, and the 1/7 occupations of the  $f$ -orbitals. This limit for the  $f$ -orbital case is about 0.14 electrons, and in the case of a 1/2 filled  $f$ -orbital, the averaging would give an occupation of 0.07. This value is taken as the limiting case for electron occupation in an atom. The figure 0.05 is

small enough to include these occupations, but large enough to exclude orbitals of lesser occupation.

It should be emphasized that our definition of an atom is one among many that may be used. As long as the atom is a subspace of Hilbert space and can be spanned by a basis set, then the theory of the previous section can be applied to it.

## 4 Illustrative calculations

### 4.1 Details of calculations

The code for calculating the bond indices outlined in the previous sections was written in the Tonto program [18]. This code evaluates all the atomic SCF calculations required to define the Roby atoms in the molecule. The molecular density matrices can also be calculated in the Tonto package, but for this paper they were calculated using the Gaussian program [47]; an interface to read the Gaussian “checkpoint” file was written to facilitate easy usage of the Tonto program.

For evaluating the bond indices, a range of test molecules was studied that would assess the applicability of the indices to chemistry. Molecules were also chosen that would allow comparison with the results obtained by other workers using other methods.

The molecules chosen included the set of first and second row hydrides and fluorides, and the hydrocarbons ethane, ethene, ethyne and benzene. A small number of related molecules were also chosen for comparison with other analysis techniques and for demonstrating trends in the bond indices.

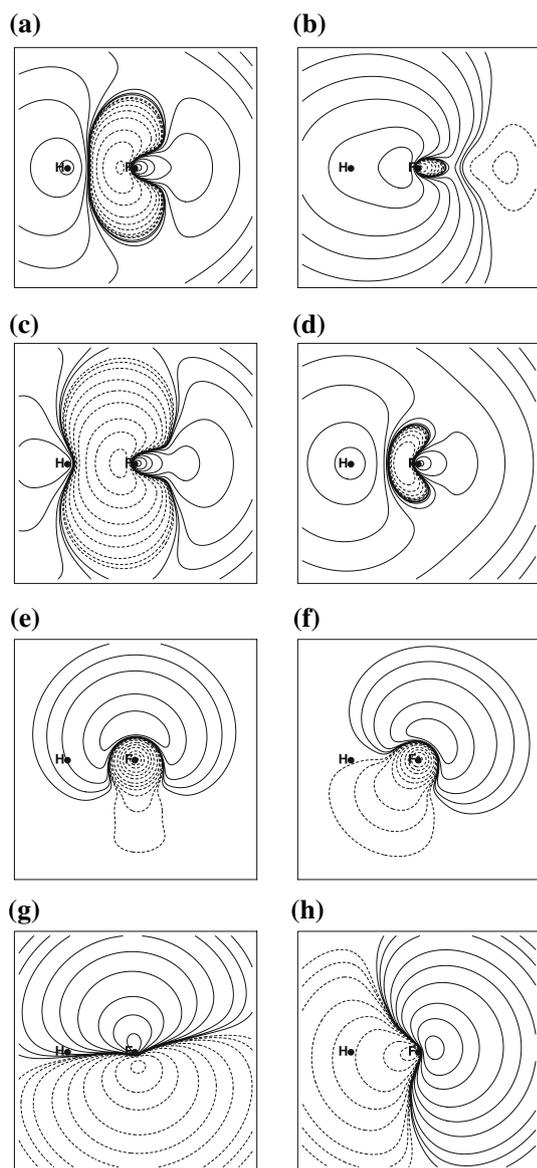
Unless otherwise stated, the test molecule geometries were optimized using Gaussian 98 [47] using double- $\zeta$  (DZP) basis sets [48,49] except for the cases of Na and Mg, where the gaussian 6-31G\* basis sets were used. The use of the Molden graphics package [50] was often helpful in these calculations.

### 4.2 The hybrid orbitals of hydrogen fluoride

As a representative example, Fig. 1 presents the hybrid orbitals for hydrogen fluoride using a 6-31G\*\* basis. Populations are also shown.

The covalent bonding and antibonding orbitals are shown, with  $\theta = 55^\circ$ . They resemble the bonding and anti-bonding orbitals that might be found in basic chemistry textbooks for the bonding or anti-bonding orbitals of diatomic molecules—but it should be made clear that these orbitals are formed simply from “unoptimized” linear combinations of the hybrid orbitals situated on each atom of the pair. These orbitals are not, for instance, energy optimized molecular orbitals.

The ionic bonding and antibonding orbitals are shown, with  $\theta = 55^\circ$ . Like the covalent anti-bonding orbitals, the



**Fig. 1** The covalent and ionic orbitals of hydrogen fluoride, using a 6-31G\*\* basis. *Solid lines* indicate positive contours, *dotted lines* are negative contours. Contour increments at 0.1 a.u. **a** covalent anti-bonding orbital,  $\theta = 55^\circ$ , **b** covalent bonding orbital,  $\theta = 55^\circ$ , **c** ionic anti-bonding orbital,  $\theta = 55^\circ$ , **d** ionic bonding orbital,  $\theta = 55^\circ$ , **e** first lone pair orbital,  $\theta = \pi/2$ , **f** second lone pair orbital,  $\theta = \pi/2$ , **g** third lone pair orbital,  $\theta = \pi/2$ , **h** fourth lone pair orbital,  $\theta = \pi/2$

ionic anti-bonding orbitals are characterised by a deficit of charge in the bonding region.

The non-bonding  $\theta = \pi/2$  orbitals are also shown, and they look like the lone-pair orbitals that might be found on an F atom. Since the single H–F bond corresponding to  $V_{\theta=55^\circ}$  is made from the 1s ANO on H, plus a linear combination of the 5 ANO's on F, there are exactly four orbitals remaining on the F atom which are exactly orthogonal to this  $V_{\theta=55^\circ}$  space.

As the orbitals are constructed entirely from the atomic projection operators, the orbitals will depend only on the bond distance between H and F within the molecule, and not on the molecular environment within which these atoms reside. Only the populations of these orbitals depend on the molecular environment.

#### 4.3 Comparing definitions of ionicity for a series of hydrides and fluorides

Tables 1 and 2 present bond indices and percent ionicities. The difference between Tables 1 and 2 is that in the former, the bond indices are calculated between single atoms, while in the latter it is calculated between groups of atoms. Thus in the former table, the bond index of  $\text{CH}_4$  is calculated between a single C atom and a single H atom, while in latter

**Table 1** Bond indices and ionicities for a series of hydrides and fluorides — bonds between *single* atoms

Mol.	A–B	$\tau_{AH}$	%I	Pauling's %I
H <sub>2</sub>	H–H	0.985	0	0
LiH	Li–H	0.938	29	24
BeH <sub>2</sub>	Be–H	0.465	8	14
BH <sub>3</sub>	B–H	0.973	0	2
CH <sub>4</sub>	C–H	0.958	2	10
NH <sub>3</sub>	N–H	0.958	8	20
H <sub>2</sub> O	O–H	0.960	16	30
HF	F–H	0.962	26	37
NaH	Na–H	0.937	24	26
MgH <sub>2</sub>	Mg–H	0.545	15	20
AlH <sub>3</sub>	Al–H	0.970	5	13
SiH <sub>4</sub>	Si–H	0.947	2	7
PH <sub>3</sub>	P–H	0.927	0	0
H <sub>2</sub> S	S–H	0.939	1	10
HCl	Cl–H	0.946	5	20
LiF	Li–F	0.938	88	52
BeF <sub>2</sub>	Be–F	0.749	75	46
BF <sub>3</sub>	B–F	1.979	56	39
CF <sub>4</sub>	C–F	1.084	7	31
NF <sub>3</sub>	N–F	0.959	4	22
OF <sub>2</sub>	O–F	0.780	2	11
F <sub>2</sub>	F–F	0.615	0	0
NaF	Na–F	0.900	89	54
MgF <sub>2</sub>	Mg–F	0.782	83	50
AlF <sub>3</sub>	Al–F	1.374	23	46
SiF <sub>4</sub>	Si–F	1.173	19	42
PF <sub>3</sub>	P–F	1.072	18	37
SF <sub>2</sub>	S–F	0.922	19	31
ClF	Cl–F	0.699	20	22

**Table 2** Bond indices and ionicities for a series of hydrides and fluorides — Bonds between groups of atoms

Mol.	A–B	$\tau_{AH}$	%I	Pauling's %I
H <sub>2</sub>	H–H	0.985	0	0
LiH	Li–H	0.938	29	24
BeH <sub>2</sub>	BeH–H	0.890	20	14
BH <sub>3</sub>	BH <sub>2</sub> –H	0.973	0	2
CH <sub>4</sub>	CH <sub>3</sub> –H	0.953	2	10
NH <sub>3</sub>	NH <sub>2</sub> –H	0.927	7	20
H <sub>2</sub> O	OH–H	0.911	14	30
HF	F–H	0.962	26	38
NaH	Na–H	0.937	24	26
MgH <sub>2</sub>	MgH–H	0.882	26	20
AlH <sub>3</sub>	AlH <sub>2</sub> –H	0.964	5	13
SiH <sub>4</sub>	SiH <sub>3</sub> –H	0.953	2	7
PH <sub>3</sub>	PH <sub>2</sub> –H	0.939	0	0
H <sub>2</sub> S	SH–H	0.937	1	10
HCl	Cl–H	0.946	5	20
LiF	Li–F	0.938	88	52
BeF <sub>2</sub>	BeF–F	0.941	74	46
BF <sub>3</sub>	BF <sub>2</sub> –F	2.701	61	39
CF <sub>4</sub>	CF <sub>3</sub> –F	2.103	58	31
NF <sub>3</sub>	NF <sub>2</sub> –F	1.019	4	22
OF <sub>2</sub>	OF–F	0.773	2	11
F <sub>2</sub>	F–F	0.615	0	0
NaF	Na–F	0.900	89	54
MgF <sub>2</sub>	MgF–F	0.899	83	50
AlF <sub>3</sub>	AlF <sub>2</sub> –F	1.636	19	46
SiF <sub>4</sub>	SiF <sub>3</sub> –F	2.763	70	42
PF <sub>3</sub>	PF <sub>2</sub> –F	1.324	16	37
SF <sub>2</sub>	SF–F	1.009	18	31
ClF	Cl–F	0.699	20	22

it is calculated between CH<sub>3</sub> and H. (The bond under consideration is indicated under “A–B”). We have reported the bond index to three decimal places to facilitate reproduction of our results.

Most of the bond indices are in accord with chemical intuition, but there are a few exceptional cases. BF<sub>3</sub> is most unusual in having a bond index of 1.979, where one might have expected a value closer to 1. The percentage ionicity shows that this is due to strong covalent and ionic bond indices. This effect might be explained by the fact that, in the definition of the Boron atomic projector, all three *p* orbitals appear, even though there is only one *p* type electron in Boron. Evidently these *p* orbitals play a quite significant role in the bond index formula we have used.

Also presented for comparison are Pauling's percent ionicities. These are calculated from Pauling's electronegativity

differences using the formula [2]

$$\% \text{ ionicity} = 1 - e^{-1/4|\chi_{AB}|}, \quad (45)$$

where  $\chi_{AB}$  is the electronegativity difference of atoms *A* and *B*.

An examination of Pauling's percent ionicities shows that for the hydrides there is an initial decrease in ionicity followed by an increase, as one moves across a row of the periodic table. Intuitively this makes sense, as one would expect the ionicity to be greater in LiH and HF, where there is a large difference in electronegativity, than in CH<sub>4</sub>, where there is not. For the fluorides, Pauling's percent ionicities show a decrease as one moves across a row of the periodic table. Both these trends in percent ionicity are reproduced by our indices.

#### 4.4 Bond-indices of some organic molecules

It is customary to examine the series of hydrocarbons ethane, ethene, ethyne and benzene when evaluating new bond order techniques, since it is in these situations that the bond orders of conventional chemistry can be unambiguously assigned. Additionally, the bonds should have 100% covalent character. The bond indices and percent covalencies for these cases are displayed in the upper part of Tables 3 and 4. The lower part of the tables has a selection of other organic molecules. (The bond under consideration is indicated under the second column “A–B”.)

The results presented in Table 3 are fully consistent with the expectations of a typical Lewis and Kekule resonance analysis of these compounds. Ethane, ethene, and ethyne have carbon-carbon bond indices of approximately one, two and three as expected. Benzene on the other hand, because of resonance, has a bond index roughly half way between that of a single bond and a double bond.

**Table 3** Bond indices and covalencies for organic molecules — bonds between single atoms

Mol.	A–B	$\tau_{AB}$	%C
C <sub>2</sub> H <sub>2</sub>	C–C	2.980	100
C <sub>2</sub> H <sub>4</sub>	C–C	2.031	100
C <sub>2</sub> H <sub>6</sub>	C–C	0.994	100
C <sub>6</sub> H <sub>6</sub>	C–C	1.587	100
N <sub>2</sub>	N–N	2.896	100
N <sub>2</sub> H <sub>2</sub>	N–N	2.005	100
N <sub>2</sub> H <sub>4</sub>	N–N	0.932	100
CO <sub>2</sub>	C–O	2.278	86
H <sub>2</sub> CO	C–O	2.078	91
HCN	C–N	2.964	99

Basis 6-31G\*\*//3-21G

**Table 4** Bond indices and covalencies for organic molecules — bonds between *groups* of atoms

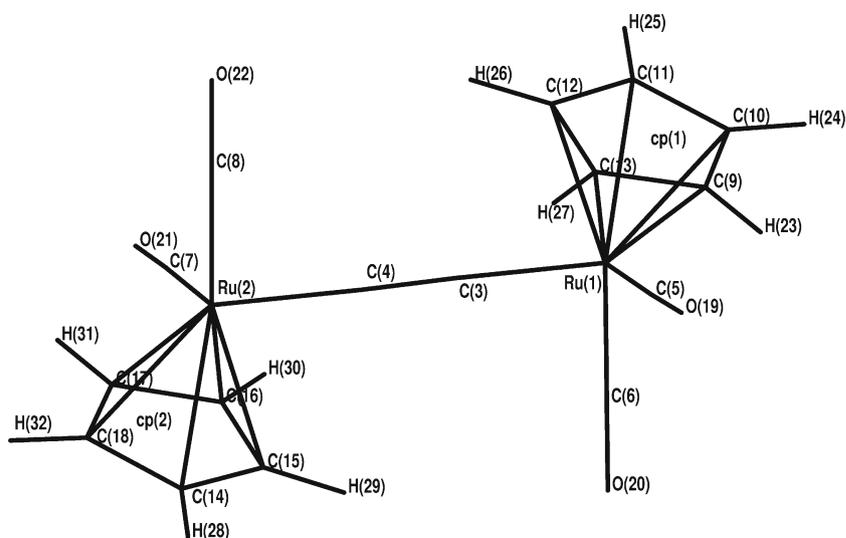
Mol.	A–B	$\tau_{AB}$	%C
C <sub>2</sub> H <sub>2</sub>	HC–CH	3.073	100
C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub> C–CH <sub>2</sub>	2.298	100
C <sub>2</sub> H <sub>6</sub>	H <sub>3</sub> C–CH <sub>3</sub>	0.963	100
C <sub>6</sub> H <sub>6</sub>	$\frac{1}{2}(\text{H}_3\text{C}_3\text{–C}_3\text{H}_3)$	1.951	100
N <sub>2</sub> H <sub>2</sub>	HN–NH	2.073	100
N <sub>2</sub> H <sub>4</sub>	H <sub>2</sub> N–NH <sub>2</sub>	1.041	100
CO <sub>2</sub>	OC–O	2.782	82
H <sub>2</sub> CO	H <sub>2</sub> C–O	2.417	85
HCN	HC–N	3.053	99

Basis 6-31G\*\*//3-21G

In Table 4 the bond indices are calculated for bonds between groups of atoms. The value for benzene was calculated by considering the bond index between two halves of the benzene molecule (as groups of atoms) and then halving the value. Using this atom-group method typically results in higher bond indices compared with those in Table 3, and in some cases e.g., benzene (1.95) and carbon dioxide (2.78) much higher indices. The bond indices calculated between single atoms in Table 3 corresponds more closely to conventional ideas of a bond index, and leads more consistently to bond indices comparable with traditional thinking.

#### 4.5 Bond-indices in metal complexes and hypervalency issues

Aside from looking at conventional systems, an organometallic system was also examined. It is in these systems where such methods for extracting bond-indices, etc. become most

**Fig. 2** The Ruthenium carbonyl,cyclopentadienyl complex

useful. The complex studied was C<sub>2</sub>(Ru(CO)<sub>2</sub>cp)<sub>2</sub> (see Fig. 2).

Geometric coordinates for the complex were determined from X-ray structure analysis of a crystal [51]. The orbitals were generated from a 3-21G basis.

The bond indices and percent covalencies for this complex are presented in Table 5. An examination of this table reveals the following bonding picture for the ruthenium complex:

1. There is negligible direct bonding between the two Ruthenium atoms.
2. The Ru(1)–cp(1) bond index is larger than that of the Ru(1)–C(9) bond index, where C(9) is a single carbon in the cp(1) ring. The Ru(1)–cp(1) bond is roughly half covalent (44%), half ionic (56%).
3. The acetylene bond is weakened from the ethyne value of 2.980 (see Table 3) to 1.592 [this is the bond C(3)–C(4)]. This is consistent with the notion that external bonding with the ruthenium atoms weakens the internal C–C bond. The carbonyl bond is similarly weakened. (Compare the bond index of C(7)–O(21) with those carbonyl bond indices in Table 3.)
4. Adjacent C–C bonds within the cp ring are 100% covalent and are approximately single bonds [ $\tau_{AB} = 1.065$  for the bond C(9)–C(10)].

#### 4.6 The dissociation of O<sub>2</sub>

Unrestricted QCISD calculations were done for the dissociation of the oxygen triplet state, and bond indices were calculated. Table 6 presents the data of these calculations. The data shows a smooth decrease in the bond index as the oxygens are pulled apart, until a bond length of 3.6419 Å at which the bond index suddenly drops to zero.

The bonds are 100% covalent. When the bond distance is close to the minimum energy bond length, there are four

**Table 5** Bond indices and covalencies for the ruthenium complex

A–B	$\tau_{AB}$	%C
Ru(1)–Ru(2)	0.037	100
Ru(1)–C(3)	0.724	86
Ru(1)–C(3)C(4)	1.364	73
Ru(2)–C(7)	0.897	77
C(7)–O(21)	1.553	97
Ru(2)–O(21)	0.033	71
Ru(2)–C(7)	0.897	77
C(3)–C(4)	1.592	100
C(3)–Ru(2)C(4)	2.010	98
O(21)–C(7)Ru(2)	2.249	93
C(9)–C(10)	1.065	100
C(9)–H(23)	0.733	89
Ru(1)–C(9)	0.219	51
Ru(1)–cp(1)	0.380	44
Ru(2)–cp(1)	0.041	30
cp(1)–cp(2)	0.008	100

Basis 3-21G

**Table 6** Bonding indices for O<sub>2</sub> at different bond lengths

Bond length	Energy	$\tau_{AB}$
1.0419	–150.0587708	1.805
1.2419*	–150.1136299	1.693
1.4419	–150.0650365	1.584
1.6419	–149.9973340	1.503
1.8419	–149.9344069	1.456
2.0419	–149.8825646	1.432
2.8419	–149.7817513	0.606
3.2419	–149.7709637	0.536
3.4419	–149.7689773	0.516
3.6019	–149.7681156	0.505
3.6319	–149.7679996	0.503
3.6419	–149.7679634	0.000

UQCISD calculations with a cc-pvtz+6d+10f basis. Bond length in Angstroms, energy in Hartree

$\theta$  angles ranging from 50° to 90°. As the bond lengths, all the angles approach 90°, at which the covalent index is zero. Due to a limited numerical accuracy, a point is reached where angles very close to 90° are indistinguishable from 90°, hence the sudden drop of the bond index to zero.

#### 4.7 Bond indices for a Diels Alder reaction

The bond indices, defined by Eq. (39), were calculated for the bonds in the Diels Alder reaction: 1,3-propadiene + ethylene

→ cyclohexene. The bond indices are presented in Table 7 for a calculation using a 6-31G\* basis. The bonds in these tables are indicated by the atoms they join, which are given in Fig. 3. ‘TS’ refers to the transition structure.

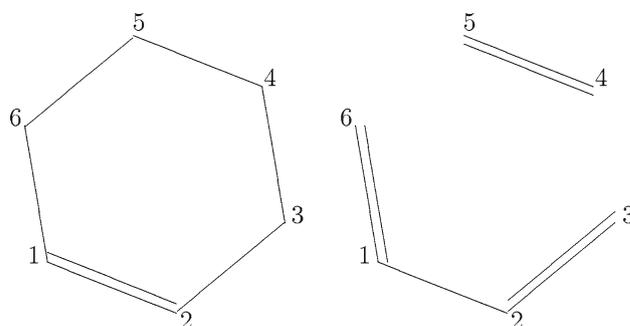
The bond indices for reactants and products agree very well with the structures drawn in Fig. 3. The bond indices for the transition structure clearly show the intermediate nature of the bonds as they are in the middle of breaking and reforming.

#### 4.8 Basis set convergence

Table 8 shows that the bond index  $\tau_{AB}$ , defined by (39), and the covalency, defined by (41), for the bonds of water and hydrogen fluoride converge with increasing basis set.

**Table 7** Bond indices  $\tau_{AB}$  for the Diels-Alder reaction: 1,3-propadiene + ethylene → cyclohexene, calculated with a 6-31G\* basis

A–B	cyclohexene	TS	diene + ethylene
1–2	1.937	1.524	1.175
2–3	1.087	1.653	1.964
3–4	1.018	0.553	0.0
4–5	1.031	1.649	2.036
5–6	1.026	0.553	0.0
6–1	1.087	1.653	1.964

**Fig. 3** Atom labelling for Cyclohexene, 1,3-propadiene, and ethylene**Table 8** The bond index  $\tau_{AB}$  and % covalency (%C) for the bonds of water and hydrogen fluoride with increasing basis set quality

Basis	$\tau_{OH}$	%C	Basis	$\tau_{HF}$	%C
<i>Water</i>			<i>Hydrogen fluoride</i>		
STO-3G	0.927	0.948	STO-3G	0.899	0.918
3-21G	0.947	0.860	3-21G	0.943	0.774
6-31G*	0.954	0.838	6-31G*	0.955	0.746
6-31G(d,p)	0.955	0.835	6-31G(d,p)	0.957	0.741

## 5 Conclusion

The concepts of chemical bonding developed in this paper are shown to be elegantly connected with the algebra and geometry of projection operators. Using these ideas we have defined a bond index, as well as covalent and ionic bond indices which are based on the expectation values of hermitian operators.

An important aspect of this work is that the definition of the ionic bond index appears on an equal footing with the covalent bond index, and both are defined by a generalisation of the bond order rule taught in elementary chemistry courses. These indices are related to each other by certain simple pythagorean relations, which enables the percentage of covalency or ionicity of a bond to be calculated. The bond indices can be calculated between atoms, or between functional groups of atoms. Furthermore, the Roby and ionic operators, which are used in defining our bond indices, are related to Araki's angle operators, and the eigenstates of these operators can be considered as "bonding", "anti-bonding" and "lone-pair" orbitals between pairs of atoms.

The formalism presented depends only on the one-electron density operator and the properties of the projection operators used to represent each atom in a molecule and hence our definitions automatically have the required invariance properties with respect to unitary mixing of basis orbitals. In addition, the results are stable with respect to basis set extension. The method is also computationally very simple to implement.

The definitions of the bond indices have been applied to a series of first and second row hydrides and fluorides, as well as to some hydrocarbons, a transition metal complex, and to the reactants, products and transition structures of a Diels–Alder reaction and a dissociative reaction for O<sub>2</sub>. The calculated covalencies and ionicities agree well with intuitive and traditional views. The bond orders mostly also agree well with intuition once an adjustment is made to the idea that bond order is not a scalar, but a two dimensional entity comprised of covalent and ionic components.

Despite the fact that the theory proposed is largely parameter free, there was one somewhat ad hoc parameter introduced to exclude certain angular subspaces from the bond-index operator. This was deemed necessary for non-diatomic systems where at least one of the atoms *A* or *B* in the pair is in close proximity to other atoms, so that charge from these nearby atoms accumulates in the lone electron pair regions so distorting the ionicity. Further work should consider how this ad hoc parameter could be eliminated from the theory. A refinement of the definition of the projection operators associated with each atom, or each pair of atoms, should also be the subject of further research. This paper has examined only a few cases in which the bond index formula we have developed could be applied. Further studies involving classic three-center two-electron bonds (as in the boranes),

or the topical issues involving quintuple bonds mentioned in the Sect. 1, are also obvious subjects for future research.

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## Appendix

**A** The eigenvalues of  $\mathcal{R}$  and  $\mathcal{I}$  come in pairs of opposite sign

To see this, we note that  $\mathcal{R}$  and  $\mathcal{I}$  anticommute, i.e.,  $\mathcal{R}\mathcal{I} + \mathcal{I}\mathcal{R} = 0$ . Then if  $|\lambda\rangle$  is an eigenstate of  $\mathcal{R}$  with eigenvalue  $\lambda$ , then  $\mathcal{I}\mathcal{R}|\lambda\rangle = \lambda\mathcal{I}|\lambda\rangle = -\mathcal{R}\mathcal{I}|\lambda\rangle$ . The last equality shows that  $\mathcal{I}|\lambda\rangle$  is an eigenstate of  $\mathcal{R}$  with eigenvalue  $-\lambda$  which proves that the non-zero eigenvalues of  $\mathcal{R}$  come in pairs of opposite sign, i.e., the eigenstates of  $\mathcal{R}^2$  with non-zero eigenvalue are doubly degenerate. A similar argument can be used to prove the same thing for  $\mathcal{I}$ .

**B** The eigenvalues of  $\mathcal{R}^2$  and  $\mathcal{I}^2$  are between 0 and 1

To prove this result let  $\psi$  be a normalized state in the subspace  $V_{AB}$ . Then

$$\langle\psi|\mathcal{I}^2|\psi\rangle = \|(P_A - P_B)\psi\|^2 \geq 0 \quad (46)$$

$$\langle\psi|\mathcal{R}^2|\psi\rangle = \|(P_A + P_B - 1)\psi\|^2 \geq 0. \quad (47)$$

But  $\mathcal{R}^2 = 1 - \mathcal{I}^2$  which yields

$$1 - \langle\psi|\mathcal{I}^2|\psi\rangle \geq 0, \quad (48)$$

from which we deduce

$$0 \leq \langle\psi|\mathcal{I}^2|\psi\rangle \leq 1 \quad (49)$$

$$0 \leq \langle\psi|\mathcal{R}^2|\psi\rangle \leq 1 \quad (50)$$

as required.

**C** The eigenstates of  $\mathcal{R}$  and  $\mathcal{I}$  are a linear combination of two basis states which extremize their mutual overlap

A state  $|a_\theta\rangle \in V_A$  which extremises its overlap into the space  $V_B$  is, by definition, an eigenstate of the operator  $P_A P_B P_A$  i.e., it is an eigentate of  $P_B$  restricted to the space  $V_A$  [3],

$$P_A P_B P_A |a_\theta\rangle = \lambda_\theta^2 |a_\theta\rangle. \quad (51)$$

Likewise, a state in the space  $V_B$  which extremises its overlap into the space  $V_A$  is an eigenstate of the operator  $P_B P_A P_B$ .

$$P_B P_A P_B |b_\theta\rangle = \mu_\theta^2 |b_\theta\rangle. \quad (52)$$

From these two equations we have

$$\langle a_\theta | P_A P_B P_A P_B | b_\theta \rangle = \lambda_\theta^2 \langle a_\theta | b_\theta \rangle = \mu_\theta^2 \langle a_\theta | b_\theta \rangle \quad (53)$$

The last two equations show that  $|a_\theta\rangle$  and  $|b_\theta\rangle$  are orthogonal (i.e.,  $\langle a_\theta|b_\theta\rangle = 0$ ) or  $\lambda_\theta^2 = \mu_\theta^2$ . In the latter case the two vectors  $|a_\theta\rangle$  and  $|b_\theta\rangle$  may be said to be “paired”. We shall consider these paired eigenstates in the following. Assuming  $\lambda_\theta \neq 0$ , it can be shown by direct substitution that

$$|a_\theta\rangle = P_A P_B |b_\theta\rangle / \lambda_\theta, \quad (54)$$

$$|b_\theta\rangle = P_A P_B |a_\theta\rangle / \lambda_\theta. \quad (55)$$

From this it is easy to show that

$$P_B |a_\theta\rangle = \lambda_\theta |b_\theta\rangle, \quad (56)$$

$$P_A |b_\theta\rangle = \lambda_\theta |a_\theta\rangle, \quad (57)$$

$$\lambda_\theta = \langle a_\theta | b_\theta \rangle \quad (58)$$

Using the definitions  $\mathcal{R} = P_A + P_B - 1$  and  $\mathcal{I} = P_A - P_B$  a little more algebra shows that

$$\mathcal{R}^2 |a_\theta\rangle = \lambda_\theta^2 |a_\theta\rangle \quad (59)$$

$$\mathcal{R}^2 |b_\theta\rangle = \lambda_\theta^2 |b_\theta\rangle \quad (60)$$

$$\mathcal{I}^2 |a_\theta\rangle = (1 - \lambda_\theta^2) |a_\theta\rangle \quad (61)$$

$$\mathcal{I}^2 |b_\theta\rangle = (1 - \lambda_\theta^2) |b_\theta\rangle \quad (62)$$

Thus  $|a_\theta\rangle$  and  $|b_\theta\rangle$  are also eigenstates of  $\mathcal{R}^2$  and  $\mathcal{I}^2$ . (This is consistent with the fact that  $\mathcal{R}^2$  and  $\mathcal{I}^2$  commute with  $P_A$  and  $P_B$ , hence they also commute with  $P_A P_B P_A$  and  $P_B P_A P_B$ ; commuting operators may share a common eigenbasis). Since the eigenvalues of  $\mathcal{R}^2$  are by definition  $\cos^2 \theta$  this proves that  $\lambda_\theta^2 = \cos^2 \theta$ . It is now easy to prove by direct substitution that the eigenstates of  $\mathcal{R}$  are

$$|\pm \cos \theta\rangle = \frac{|a_\theta\rangle \pm |b_\theta\rangle}{\sqrt{2(1 \pm \cos \theta)}}. \quad (63)$$

The eigenstates of  $\mathcal{I}$  may also be shown to be given by

$$|\pm \sin \theta\rangle = \frac{1}{\sqrt{2}} (|+\cos \theta\rangle \pm |-\cos \theta\rangle). \quad (64)$$

This proves that the eigenstates of  $\mathcal{R}$  and  $\mathcal{I}$  may be expressed as a linear combination of only two states  $|a_\theta\rangle$  and  $|b_\theta\rangle$  which extremise their mutual overlap. The eigenstates of  $\mathcal{I}$  are related to the eigenstates of  $\mathcal{R}$  by a rotation of  $\pi/4$ , and so they span the same two dimensional subspace  $V_\theta$ .

**D** The eigenstates of  $\mathcal{R}^2$  (respectively  $\mathcal{I}^2$ ) have maximum and minimum shared population (respectively ionic population)

It has been stated that the covalent bonding and anti-bonding orbitals give maximum and minimum shared populations on an angle eigenspace  $V_\theta$ . Similarly the ionic bonding and anti-bonding orbitals give the maximum and minimum difference populations on  $V_\theta$ . Here we quantify and prove this result.

To proceed, we must first provide a general definition of what is meant by the terms “shared population” and “ionic population” of an orbital. If  $Q$  is either the Roby operator,

$R$ , or the ionic operator,  $I$ , both of which are hermitian and commute with  $P_\theta$ , the projector onto the angle eigenspace  $V_\theta$ , then the  $Q$ -electron population of angle eigenspace  $V_\theta$  is defined by

$$q_\theta \equiv \text{Tr}[P_\theta Q \rho], \quad (65)$$

Note that if  $Q$  is the Roby operator  $R$ , then  $q_\theta = c_\theta$ , while if  $Q$  is the ionic operator  $I$ , then  $q_\theta = i_\theta$ . Using the fact that  $Q$  commutes with  $P_\theta$ , and  $P_\theta^2 = P_\theta$  it is easily shown that

$$q_\theta = \text{Tr}[Q P_\theta \rho P_\theta] = \text{Tr}[Q \rho_\theta] = \frac{1}{2} \text{Tr}[\{Q, \rho_\theta\}]. \quad (66)$$

where  $\{Q, \rho_\theta\}$  is the anti-commutator of  $Q$  and  $\rho_\theta$ ,  $\{Q, \rho_\theta\} = Q \rho_\theta + \rho_\theta Q$ .  $\rho_\theta$  is defined by the second equality above, while the cyclic property of the Trace has been used to get the final equality. Unlike  $Q \rho_\theta$  or  $\rho_\theta Q$ ,  $\{Q, \rho_\theta\}$  is a self-adjoint operator. The population  $q_v$  of an orbital  $v \in V_\theta$  can then be written as

$$q_v \equiv \langle v | \frac{1}{2} \{Q, \rho_\theta\} | v \rangle \quad (67)$$

Using the above definition, we now prove that the covalent (respectively, ionic) bonding and anti-bonding orbitals give maximum and minimum shared (difference) populations on  $V_\theta$ . The orbitals in  $V_\theta$  giving extreme values of  $\langle v | Q | v \rangle$  on  $V_\theta$  are precisely the eigenstates  $v_\pm$  (corresponding to eigenvalues  $\pm q$  resp.) of  $Q$  on  $V_\theta$ . It follows that these eigenstates will also give the maximum and minimum values of (67) provided  $Q$  and  $\{Q, \rho_\theta\}$  commute on  $V_\theta$ , a fact which is now demonstrated. Since on  $V_\theta$ ,  $Q$  has eigenvalues  $\pm q$ , it follows that  $Q^2$  reduces to a scalar  $q^2$  multiple of the identity on  $V_\theta$ . Hence on  $V_\theta$  we have

$$Q \{Q, \rho_\theta\} = Q(Q \rho_\theta + \rho_\theta Q) \quad (68)$$

$$= q^2 \rho_\theta + Q \rho_\theta Q \quad (69)$$

$$= (Q \rho_\theta + \rho_\theta Q) Q \quad (70)$$

$$= \{Q, \rho_\theta\} Q, \quad (71)$$

so that  $Q$  and  $\{Q, \rho_\theta\}$  commute, which is sufficient to prove the result.

**E** The bond index in terms of the covalent and ionic bond indices, on a particular paired  $\theta$  eigenspace,  $V_\theta$

To motivate the definition for the bond index, consider the eigenstates of  $\rho$  on  $V_\theta$ . As already mentioned, these will be the orbitals that have maximum or minimum occupation numbers in the space  $V_\theta$ . Using the covalent bonding and anti-bonding orbitals as basis, the matrix representation of  $\rho$  is

$$\langle c_\theta | \rho | c_\theta \rangle = \begin{pmatrix} \frac{1}{2} \langle 1 \rangle + \langle s_z \rangle \langle s_x \rangle - i \langle s_y \rangle \\ \langle s_x \rangle + i \langle s_y \rangle \frac{1}{2} \langle 1 \rangle - \langle s_z \rangle \end{pmatrix}, \quad (72)$$

where

$$|c_\theta\rangle = \begin{pmatrix} | + \cos \theta \rangle \\ | - \cos \theta \rangle \end{pmatrix} \equiv \begin{pmatrix} |c_\theta^+\rangle \\ |c_\theta^-\rangle \end{pmatrix} \quad (73)$$

and where we have used the definitions of the hybrid spin operators, and also, for example,

$$\langle c_\theta^+ | \rho | c_\theta^- \rangle = \text{Tr}(\rho |c_\theta^-\rangle \langle c_\theta^+|) = \langle |c_\theta^-\rangle \langle c_\theta^+| \rangle. \quad (74)$$

The expectation values in (72) are taken over the space  $V_\theta$ . The eigenvalues of  $\rho$  are given by [52]

$$n_\tau^\pm = \frac{1}{2} \langle 1 \rangle \pm \sqrt{\langle s_x \rangle^2 + \langle s_y \rangle^2 + \langle s_z \rangle^2}. \quad (75)$$

These eigenvalues are, in fact, the maximum and minimum total populations that are obtainable within space  $V_\theta$ . The expectation of  $s_y$  can be deleted in the above expression as  $s_y$  is self-adjoint and pure imaginary, hence its expectation is zero. The eigenstates are thus

$$|\tau_\theta^+\rangle = \frac{1}{\sqrt{\zeta_\theta^2 + 1}} (|c_\theta^+\rangle + \zeta_\theta |c_\theta^-\rangle), \quad (76)$$

$$|\tau_\theta^-\rangle = \frac{1}{\sqrt{\zeta_\theta^2 + 1}} (\zeta_\theta |c_\theta^+\rangle - |c_\theta^-\rangle). \quad (77)$$

where

$$\zeta_\theta = \frac{\langle s_x \rangle}{\langle s_z \rangle + \sqrt{\langle s_x \rangle^2 + \langle s_z \rangle^2}}. \quad (78)$$

By analogy with the covalent and ionic bond indices, the bond index on  $V_\theta$  is defined as

$$\tau_\theta = \frac{1}{2} (n_\tau^+ - n_\tau^-). \quad (79)$$

It can be deduced from this that

$$\tau_\theta = \sqrt{c_\theta^2 + i_\theta^2}. \quad (80)$$

Thus on  $V_\theta$ , the bond index  $\tau_\theta$  is a pythagorean sum of the covalent and ionic bond indices.

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