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REPLY TO COMMENT

How to properly compute the resonance energy within the ab initio valence bond theory: a response to the ZHJVL paper

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Abstract Valence bond (VB) theory describes a conjugated system by a set of electron-localized Lewis resonance structures. VB assumes that the magnitude of the intramolecular electron delocalization can be measured in terms of a resonance energy (RE), taken to be the energy difference between the real conjugated system (delocalized) and the corresponding most stable virtual resonance structure (localized). Proper RE estimates within VB theory require both delocalized and localized states to be defined at the same theoretical level, and the definition of the localized state to closely correspond to the intuitive picture of the corresponding VB structure. In contrast, the VB-delocal and VB-local computational approaches adopted by Zielinski, et al. [preceding paper in this issue] used definitions for either the delocalized or the localized states which, in our view, depart from the intuitive chemical picture. Consequently, their RE estimates are much lower than seemingly appropriate experimental evaluations with which they strongly disagree. Very large basis sets approaching completeness blur the boundaries among resonance structures and result in "basis set artifact" problems within any variant of VB theory. However, block-localized wavefunction (BLW) computations with mid-size basis sets not only exhibit insignificant variations with theoretical levels, but the resulting RE estimates also are justified by comparisons with those employing experimental data and MO computations. We stress that RE differs from the aromatic stabilization energy (ASE). The RE measures the total stabilization of an aromatic system, whereas ASE measures only the part of the RE that exceeds that of appropriate conjugated (but non-aromatic) reference molecules.

Keywords Valence bond theory · Resonance energy

1 Introduction

The concept of resonance energy (RE) originates from the valence bond (VB) theory developed by Hückel, Pauling, Wheland and other pioneers around 80 years ago [1–6]. The RE is a measure of the magnitude of contributions from resonance structures other than the principal Lewis structure to the ground state of a conjugated molecule. Benzene is the classical example. Its extraordinary chemical and thermodynamic stability, rationalized initially by a description in terms of two equivalent Kekulé structures, characterizes "aromaticity." Despite its virtual nature, aromaticity remains one of the most important concepts in chemistry. Countless efforts to characterize and to evaluate aromaticity based on reactivity, energetic, geometric, electronic, magnetic, and other spectroscopic (IR and UV) criteria have continued for nearly one century [6–22]. VB and resonance theory provided the sustained conceptual basis, which became a cornerstone of chemical

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understanding [23–25]. Hückel MO theory was not widely applied until the late 1940s, and ab initio computations and issues such as basis set artifacts (of concern in this paper) were far in the future. But modern computational capability allows concepts to be examined quantitatively with far more flexibility than that afforded by using available thermochemical data. Since RE's are not directly measurable experimentally, estimations are arbitrary in the sense that they depend on the method (and the data) devised for this purpose. Consequently, many diverse and sometimes dramatically different empirical treatments and computational techniques have been employed. But many of the various approaches are not free from discernable flaws, improper choices of reference compounds, and conceptual differences in the nature of the energy being evaluated (e.g., RE vs. the aromatic stabilization energy (ASE) [26, 27]). When these considerations are taken into account, RE estimates should and do agree at least to a reasonable extent (see Refs. [28, 29]). Since a very large number of various types of RE evaluations of aromatic systems exist, notably for benzene [4, 22, 29–53], it is reasonable to expect that newly proposed RE estimates would be compared with the most sophisticated literature values and differences reconciled. While experimental thermochemical data have been employed widely to derive empirical resonance energies, no entirely "perfect" method exists. Nevertheless, if care is taken to avoid "contaminating" effects and to include appropriate corrections for well-recognized imperfections, RE estimates converge to quite similar values [28, 29, 52, 54–56]. If the results of a proposed method deviate from such "best" REs, the reasons should be understood and rationalized. Science speaks with data. Computational findings always should be scrutinized by comparison with the most refined experimental evidence, directly or indirectly.

In the preceding paper, Zielinski et al. [58] (ZHJVL in short hereafter) present (in our view) misleading computations of the REs of benzene and of a completely hypothetical H_6 ring (with HH distances constrained to be the same as in H_2) [52–60] purported to show the alleged relatively large basis set dependency of the BLW method. ZHJVL cited Mo's 2009 paper [54], but failed to address his detailed analysis of their earlier work [52, 60], which already showed why both ZHJVL's sets of energy and structural data are difficult to reconcile with experimental facts. ZHJVL's benzene VRE estimates, 20–32.5 kcal/mol, are more than 50 kcal/mol smaller than those based on sophisticated analyses of experimental and computational data [28, 54]. ZHJVL concede that their data "differ significantly from the literature values" but no analysis or justification of the discrepancies is offered.

We argue that basis set sensitivity lies at the core of VB theory, rather than being specific to its simplest variant, BLW. Such "basis set artifacts" can influence VB-based methods generally, when large basis sets approaching the completeness limit are employed. We show even more extensively than before [54] that the minor BLW data variability is inconsequential in typical applications employing medium-sized basis sets of the polarized DZ and TZ types.

VB theory centers on the individuality of atoms within molecules and defines a chemical bond as the overlap of atomic orbitals on two bonding atoms. In the early days of theoretical chemistry, it was assumed that each AO could be described by a single Slater-type orbital (STO), which is compact and satisfies the nuclear cusp condition. But the computational complexity involved in the multi-center integrals with original STO functions and the inaccuracy of computations using minimal STO-nG basis sets prompted the use of contracted GTO split valence basis sets with polarization and diffuse functions. This improvement did not change the philosophy of VB methods, since as long as the one-electron orbitals in VB calculations are optimized and used as AOs, ab initio VB calculations should be just like those with STOs. This approach is exhibited richly in modern VB-Self-Consistent-Field (VBSCF) [61, 62] and breathing-orbital VB (BOVB) computations [63–66]. However, infinite one-center basis sets (when used to describe an entire molecule) are unphysical as they negate the concept of atoms in molecules and thus the philosophy of VB theory. Our extensive applications have demonstrated abundantly that basis sets of up to mid-size generate consistent results for REs and structural parameters; moreover, the results are supported by a considerable number of comparisons based on experimental and MO-based computational evidence [54, 67–71]. The relative basis set invariability of Zielinski et al.'s results with very large basis sets, whose origin is explored below, does not justify nor legitimize the use of inappropriate versions of VB theory in the computations of REs generally. Especially so, when their computations are inconsistent with both experimental and other theoretical evidence and clearly underestimate RE's.

We now clarify the strategy for computing RE within the VB theory, illuminate how to accommodate conventional VB concepts in modern ab initio computational chemistry, and vindicate our fundamental disagreement with ZHJVL's techniques. The actual extent of basis set dependency in VB calculations also is documented.

2 The concept of resonance

Before presenting and comparing numerical computations, we specify our views of the concept of resonance [72]. In VB as in conventional theory, a single covalent Lewis structure where electrons are paired between two bonding atoms or are on individual atoms ("lone pairs") may suffice to describe the electronic structure, geometry, and properties of a "classical" ("localized") molecule adequately. However, when this is not the case, e.g., for "delocalized" conjugated and aromatic systems such as benzene, the VB formalism invokes other Lewis or "resonance structures," both covalent and ionic, which contribute to a "resonance hybrid" providing a much more accurate description. The Rumer spin coupling patterns [73, 74] determine the total number (M) of independent resonance structures. Wheland [6] summarized empirical rules to identify the important resonance structures for a conjugated molecule by assuming that a covalent bond is usually more stable than an ionic bond. The resonance energy (RE) is defined by its derivation, "by subtracting the actual energy of the molecule in question from that of the most stable contributing structure" [5]. In VB theory, the wavefunction for a resonance structure K (for simplicity assuming closed-shell cases, i.e., $N = 2n$) is defined by a Heitler-London-Slater-Pauling (HLSP) function as [23–25]

$$\Phi_K = N_K\hat{A}\left\{(\varphi_1\varphi_2\varphi_3\ldots\varphi_N)\prod_{ij}[\alpha(i)\beta(j)-\beta(i)\alpha(j)]\right\} \tag{1}$$

where N_K is the normalization constant, $\hat{A}$ is an antisymmetrizer. In the above resonance structure K, two electrons on orbitals φ_i and φ_j form a chemical bond. As a consequence, the overall molecular wavefunction Ψ is a superposition of all independent configurations

$$\Psi = \sum_{K=1}^{M} C_K\Phi_K \tag{2}$$

If we assume that the resonance structure L is the most stable (i.e., has the greatest weight) among all resonance contributors, the RE would be

$$\mathrm{RE} = E(\Phi_L) - E(\Psi) \tag{3}$$

This general knowledge of VB theory, inherited from the pioneers, has been well recognized by all subsequent generations of chemists. However, controversy and confusion arose when theoretical chemistry evolved into the ab initio computational era, characterized by MO-based methods. Note that Pauling and Wheland were not personally involved in the development of modern computational chemistry, particularly in the renascence of the ab initio VB approaches since mid-1980s [23, 49, 51, 63, 75–85]. The central issue in this paper is how to compute the RE with VB theory employing modern computational chemistry with the seemingly well-defined Eq. 3.

All modern ab initio methods (including ab initio VB methods) are capable of computing geometries and energies of adiabatic states (namely Ψ), which can be compared with experimental data. But all computational methods are labeled with their theoretical levels (including the electron correlation treatment), which designate the approximations employed in the approaches toward solving the Schrödinger equation.

The VB description of a molecule as a collection of local bonds can be made clearer by expressing the HLSP functions Φ_K in terms of bond functions, defined as

$$\varphi_{ij} = \hat{A}\{\varphi_i\varphi_j[\alpha(i)\beta(j)-\beta(i)\alpha(j)]\} \tag{4}$$

Then, Eq. 1 can be rewritten as

$$\Phi_K = N_K\hat{A}(\phi_{12}\phi_{34}\ldots\phi_{n-1n}) \tag{5}$$

This HLSP function can be simplified dramatically, while still retaining the VB characteristics of localization, by making the two bonding orbitals φ_i and φ_j equal (i.e., doubly occupied) but strictly localized within their bonding area. Note that the bond function, which embraces the concepts of the electron pair, the chemical bond, the pure bond state, and resonance among pure bond states was introduced by Slater in 1931 [86]. The use of doubly occupied bond functions reduces Eq. 5 to only one Slater determinant, compared with the original combination of 2^n Slater determinants. A general extension of this idea results in the BLW method [70, 71], where all primitive orbitals and electrons are partitioned into L blocks (or groups), and each MO is allowed to expand only in one block. While block-localized MOs (BL-MOs) in the same block are constrained to be orthogonal, BL-MOs between different blocks are non-orthogonal. In such a way, Eq. 5 can be reduced to a form

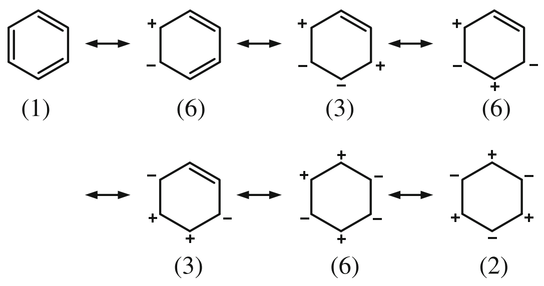
$$\Phi_K = N_K\hat{A}\{\Omega^1\Omega^2\cdots\Omega^L\} \tag{6}$$

where Ω^A is a successive product of n_A occupied spin-orbitals in subgroup A

$$\Omega^A = \psi_1^A\alpha\psi_1^A\beta\cdots\psi_{n_A/2}^A\beta \tag{7}$$

Clearly, the simplification in going from Eqs. 5 to 6 sacrifices the electron correlation. ZHJVL characterized BLW by "one-electron basis" and VB by "n-electron basis" descriptions, when, in reality, both their and our work used one-center GTO basis sets throughout; no electron–electron distances were implicated in the basis functions [58]. The major difference between VB and BLW lies in the electron correlation. But since the RE is the energy difference between the most stable resonance structure and the adiabatic state, the influence of electron correlation (which is present in both) tends to balance. Thus, the influence of electron correlation on RE is secondary. Our previous calculations using both ab initio VB and BLW confirmed that electron correlation plays a minor role in the computations of such electron delocalization energies [87, 88]. This claim is in accord with many findings [89, 90] that some HF relative energies such as rotamer or isomer energy differences for small and stable molecules are very close to those from high-level computations. Furthermore, the extension of the BLW to DFT levels incorporates electron correlation effects at least to some extent [71]. We also note that ZHJVL implied that resonance and delocalization are two different concepts by concluding that "the valence bond approach employs a Pauling–Wheland resonance energy and that the block-localized approach employs a delocalization criterion" [58]. Note that Wheland conceded that RE could also be spoken of as delocalization energy [6, 72]. In our usage, "delocalization" includes smaller electron transfer effects such as hyperconjugation [91] and is a broader term than "resonance." But in ZHJVL's benzene and H_6 cases, these two terms are used interchangeably as the focus is on the π or σ conjugation.

In the first stages of development, VB functions were constructed from atomic orbitals, which were presumably in the form of STOs. When ab initio VB methods finally emerged with the advance of computational technology in the 1970s, it became feasible to reexamine and rethink resonance theory at the ab initio level. VB calculations with pure atomic orbitals $\{\chi\}$ as one-electron orbitals usually are labeled "classical" and each subsequent HLSP function corresponds to a VB resonance structure, or a VB structure for short. Classical VB calculations with modern methods [61–66] can be quite accurate; however, it was soon recognized that taking both the covalent and ionic components of each bond into account is essential to obtain satisfactory accuracy. Thus, even a non-polar bond like H–H should be described with three VB structures, one covalent and two ionic. For benzene, one reference Kekulé molecule (a hypothetical 1,3,5-cyclohexatriene) is described by $3^3 = 27$ VB structures (the number of equivalent structures are given in parentheses below).



Reconstruction of the total wave function for the ground state of benzene, with its two Kekulé structures and three Dewar structures, gives a total of 175 VB structures. Surprisingly, using minimal basis sets and all possible 175 resonance structures, Norbeck et al. [92] and Tantardini et al. [47] demonstrated that the five covalent Kekulé and Dewar structures contribute less to the ground state of benzene than the remaining 170 ionic structures. Since the covalent functions cannot represent benzene satisfactorily, Norbeck and Gallup eventually computed VRE = 61.4 kcal/mol by taking all relevant VB structures, 27 for the reference Kekulé structure and 175 for the delocalized ground state into account, though we will show in the following that this value is still underestimated due to the imperfection of basis sets at that time.

Complementing Norbeck and Gallup's study, one of us [93, 94] showed further that the covalent-only description of benzene not only is very poor but also that delocalized systems are, as a rule, *more ionic* than localized ones. For example, the weights of the reference Kekulé structure were 51% covalent and 49% ionic, whereas the cumulated weights of the covalent Kekulé and Dewar structures for the ground state of benzene sum to only 33%. This means that if only covalent structures are retained, the description of benzene is even poorer than that of the reference Kekulé structure. Thus, the ground state of benzene will be disfavored relative to the reference Kekulé structure; a severe underestimation of the resonance energy is the obvious consequence. This explains why the VRE's calculated to be only 32.5 kcal/mol or less by ZHJVL at the so-called "VB-local level," are much too low. Of course, the VB-local calculations, which use pure atomic orbitals, are not limited to minimal basis sets. Although ZHJVL employed a series of basis sets ranging from medium to very large, their computations were still of the classical VB type and failed to consider ionic contributors. Only covalent structures were included both in their benzene and Kekulé computations, as a consequence the RE's are strongly underestimated.

Unlike classical ab initio VB precedents, modern ab initio VB methods (e.g., GVB [95], SCVB [85], or VB-delocal in the ZHJVL paper [58]) deal with one-electron orbitals, which are allowed to delocalize during their self-consistent optimization. Usually, the orbitals are expanded in all basis functions $\{\chi_\mathrm{i}\}$ of the molecule like MOs and called overlap-enhanced orbitals (OEOs) [85, 95]

$$\varphi_i = \chi_i + \sum_{j\neq i} \lambda_{ij}\chi_j \tag{8}$$

The OEOs are a direct extension of the Coulson–Fischer orbitals for diatomic molecules [96, 97]. The advantage of such MO-like orbitals is that most of the correlation energy can be recovered with only a small number of VB structures. For instance, using five formally covalent structures, Cooper, Gerratt, and Raimondi [49] were able to recover as much as 93% of the correlation energy of benzene. Thus, OEOs play a significant role in the construction of a compact wavefunction independent of increases in the size of basis sets [23]. Note that these statements only apply to the delocalized state Ψ. However, if we were to use OEOs for the reference state Φ_L, e.g., the hypothetical 1,3,5-cyclohexatriene reference state of benzene, the orbitals of the Φ_L VB structure would delocalize significantly and the clear correspondence with the bonding scheme of the original reference VB structure would be lost. As a consequence, the OEO-modified Φ_L would then represent a "cross-bred" form intermediate between the true reference VB structure and the ground state. This is seen clearly in the ZHJVL paper, where the geometry optimization of the reference Kekulé structure at the VB-delocal level leads to a "cross-bred" geometry with partially alternating C–C bond lengths (1.369 and 1.433 Å) [52]. These are not "close to the bond lengths found in for example 1,3-butadiene," but in fact lie half-way between the alternating CC bond lengths of butadiene (1.337 and 1.476 Å) and the single (ca. 1.40 Å) CC length of benzene. As a consequence of the ZHJVL definition of the Kekulé structure, the energy of the "cross-bred" Φ_L is intermediate between that of benzene and the true energy of the reference Kekulé structure. This accounts for ZHJVL's unrealistically low benzene VRE estimates. Their 20 kcal/mol $E_{\mathrm{VRE(VB\text{-}delocal)}}$ values are even smaller.

To balance the advantages and disadvantages of the delocalized OEOs and localized AOs described above, one of us has proposed a semi-delocalized one-electron orbital type, namely bond-distorted orbitals (BDOs), which are expanded with the basis functions centered on two bonding atoms [98]. By adopting BDOs as one-electron orbitals and employing only one VB structure, we can achieve nearly the identical energy derived from a VB-CI calculation with all 27 Heitler-London VB structures shown for the hypothetical 1,3,5-cyclohexatriene. Thus, whereas delocalized OEOs allow the derivation of a compact expression for the ground state of a conjugate system with most of the electron correlation taken into account, localized BDOs are essential to derive the appropriate electron-localized reference state, namely a Lewis structure whose bonds resemble those in actual molecules. Similar self-consistent localized orbitals have been used in ab initio VB studies of resonance in carboxylic acids and enols, as well as in formamide and thioformamide [99, 100]. Obviously, the BLW method, which limits the expansion of block-localized orbitals, is conceived in the same spirit as the BDOs.

Having specified the proper use of Eq. 3, we now address the geometry issue, i.e., whether the electron-localized reference state Φ_L takes the same geometry of the electron-delocalized state Ψ. Kistiakowsky's seminal experimental estimation of the 36 kcal/mol RE of benzene was based on the heats of hydrogenation of benzene and cyclohexene, as shown in Fig. 1; [101, 102].

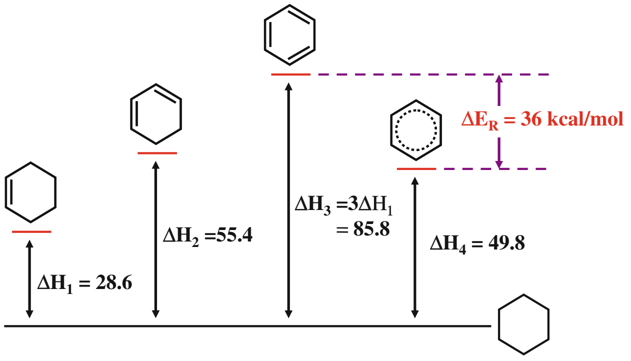


Fig. 1 Kistiakowsky's [101, 102] "historical" evaluation of the 36 kcal/mol empirical resonance energy (ΔE_R) of benzene based on heats of hydrogenation (also see Eq. 13). Note that the consequences of the very large hyperconjugation imbalance were not appreciated in 1936. The hyperconjugation-corrected empirical resonance energy of benzene ($\Delta E_{\mathrm{RCORR}}$) is about 69 kcal/mol [28, 29]

Wheland [6], Mulliken and Parr [57] as well as Coulson and Altmann [103] and later Kollmar [48] pointed out that comparisons of computational data with empirical (experiment-based) values should take into account the considerable differences in the geometries of benzene (with equal CC lengths) and of the hypothetical (Kekulé) 1,3,5-cyclohexatriene (with alternating CC lengths). In particular, CC bond "compression" (distortion) energy (ΔE_C) must be involved if the computations are performed using the benzene geometry. Hence, two kind of REs can be defined, the vertical resonance energy (VRE [51, 57], or quantum mechanical resonance energy QMRE [50, 103, 104]) where the Kekulé structure retains the geometry of benzene with all carbon–carbon bond lengths about 1.40 Å, and the adiabatic resonance energy (ARE [48, 53], also called the thermochemical resonance energy TRE [46, 50–52, 105]) where the Kekulé structure has an optimal bond-alternating geometry. Both kinds of REs are related, as shown in Fig. 2, by Eq. 9.

$$\mathrm{ARE} = \mathrm{VRE} - \Delta E_C \tag{9}$$

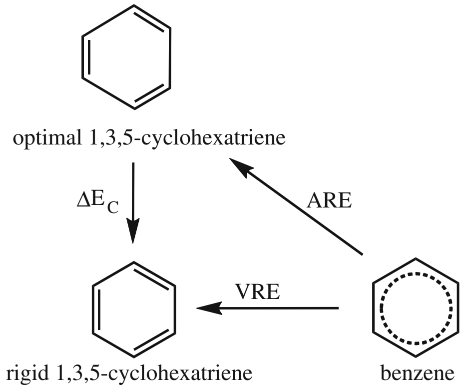


Fig. 2 Definition of the VRE and ARE relationship of benzene

Wheland [6], Mulliken and Parr [57], Coulson and Altmann [103], and Kollmar [48] all estimated the compression energy (ΔE_C) to be about 30 kcal/mol, a realistic value that can be verified easily using modern computational chemistry tools and models of ethylene and ethane [54].

The hypothetical "optimal" 1,3,5-cyclohexatriene has the alternating C=C and C–C bond length geometry expected in the absence of all π conjugation. The hypothetical "rigid" 1,3,5-cyclohexatriene has the same geometry as benzene, but the entire π conjugation among the C=C bonds has been disabled. The ΔE_C term is a measure of the "compression" (deformation) energy (ca. 30 kcal/mol) [6, 48, 54, 57, 103] required to distort the non-resonating "optimal" to the non-resonating "rigid" geometry. As a consequence, the vertical resonance energy (VRE) is much larger than the adiabatic resonance energy (ARE), since the latter includes the unfavorable compression energy (Eq. 9). Note that neither VRE nor ARE measure the "aromatic stabilization energy (ASE)" [26, 27]. ASE involves a conceptually different hypothetical 1,3,5-cyclohexatriene model, in which the C=C double bond conjugation is like that in acyclic polyenes, but the energetic advantages of the cyclic electron delocalization associated with aromaticity are absent. The energies of such "conjugated but not aromatic" cyclohexatriene models have been deduced using a number of simulation strategies (e.g., involving 1,2- or 1,4-dimethylenecyclohexadienes as well as acyclic polyenes; also see Eqs. 11, 12, and the discussion below) [26–29, 106].

The fact that VRE of benzene must be around 30 kcal/mol larger than its ARE contradicts ZHJVL's VRE values, which range from 20.0 kcal/mol at the VB-local level to 32.5 kcal/mol at the VB-delocal level. If these ZHJVL VRE values were reflecting the available experimental data, the ARE of benzene would be near zero or even negative.

ZHJVL state that the "Pauling–Wheland and Pauling–Sherman approaches [4] are two completely different ways to consider the extra stabilization energies of aromatic compounds." We agree, but also stress that the Pauling–Wheland paper does not provide an independent numerical estimate of the stabilization energy of benzene. It was concerned inter alia with Hückel-like theoretical analyses, e.g., of the contributions of various canonical structures to "the normal state of the benzene molecule". However, the energies only were deduced in terms of "α," which was not quantified theoretically. Recourse to evaluations of α by comparisons with thermochemical evaluations (in particular, of benzene itself by Pauling–Sherman data), which "may not be very reliable," does not constitute a separate determination. Moreover, there is a conceptual difference. Pauling–Wheland is a VRE method, whereas Pauling–Sherman evaluates ARE. The results of both methods are related by ΔE_C (see Eq. 9; Fig. 2), but this was not taken into account in the attempted numerical evaluation of the energy corresponding to α.

In contrast to Pauling–Wheland, the Pauling–Sherman method [107] estimated quantitative ARE's (as defined in Fig. 1) entirely empirically as the difference between the atomization energies based on experimental data for the real molecule (e.g., benzene) and the atomization energies for a model "represented by a single electronic structure" (e.g., a hypothetical non-aromatic cyclohexatriene without any conjugation among the C=C bonds). The latter was obtained from the sum of the bond energies derived from data for aliphatic compounds (e.g., 6 C–H + 3 C–C + 3 C=C bonds). Using bond energies based on experimental data available in 1933, Pauling and Sherman deduced the empirical ARE of benzene to be 39.4 kcal/mol. They expressed caveats concerning this procedure, e.g., because of "some arbitrariness in the choice of bond energies, arising from uncertainty in the experimental data, lack of constancy of bond energies from compound to compound, and other causes." Note that all C–H and C–C single bonds were assumed to have the same energy, irrespective of the carbon hybridization. Exner and Schleyer's 2001 critical reexamination refined theoretical bond energies (BE) [108]. If the same assumptions are made as Pauling–Sherman, the revised benzene ARE evaluation with the Schleyer-Exner BEs is 60.6 kcal/mol, very close to the BLW values in Tables 1 and 2.

Most earlier and current computational studies of aromaticity are based on MO approaches, where all orbitals are delocalized and thus complicate rational definitions of VB-like electron-localized reference states. Instead, real molecules typically are chosen as references and various isodesmic and homodesmotic model reactions [27, 109–111] have been employed to estimate RE's and aromatic stabilization energies (ASEs). But it has been emphasized that the intrusion of "contaminating" effects in the reference systems, such as strain, hyperconjugation, Coulomb repulsion, and hybridization imbalance, as well as uncompensated van der Waals attractions ("protobranching"), results in a wide range of REs and ASEs for the same molecule in the literature [28, 29, 106, 112–114]. However, the discrepancies in the various evaluations can be reconciled and explained when the complicating effects are taken into account and the imbalances corrected [19, 29].

Note in particular that the ASE of benzene does not correspond either to its VRE or to its ARE as defined above (see Fig. 2). ASE measures the "special" or "extra" energetic stability of benzene relative to appropriate conjugated but non-aromatic systems, typically open polyene archetypes, which do not benefit from cyclic electron delocalization. Therefore, ASE is the difference in energy

Table 1 Optimal structural parameters (bond lengths in Å) of benzene and 1,3,5-cyclohexatriene and resonance energies (kcal/mol) at the HF level

Basis set	Structure	R_1	R_2	VRE	ARE	ΔE_c
6-31G(d)	Benzene	1.386	1.386	87.87	55.11	32.76
	1,3,5-cyclohexatriene	1.316	1.517			
6-311+G(d,p)	Benzene	1.386	1.386	91.57	57.51	34.06
	1,3,5-cyclohexatriene	1.314	1.522			
cc-pVTZ	Benzene	1.383	1.383	90.65	58.89	31.76
	1,3,5-cyclohexatriene	1.311	1.515			
aug-cc-pVTZ[a]	Benzene	1.383	1.383	78.98	51.40	27.58
	1,3,5-cyclohexatriene	1.313	1.504			

[a] This basis set is less suitable for BLW computations. See text

Table 2 Optimal structural parameters (bond lengths in Å) of benzene and 1,3,5-cyclohexatriene and resonance energies (kcal/mol) at the B3LYP DFT level

Basis Set	Structure	R_1	R_2	VRE	ARE	ΔE_c
6-31G(d)	Benzene	1.397	1.397	88.76	61.79	26.97
	1,3,5-cyclohexatriene	1.329	1.528			
6-311+G(d,p)	Benzene	1.395	1.395	92.19	63.15	29.04
	1,3,5-cyclohexatriene	1.325	1.523			
cc-pVTZ	Benzene	1.391	1.391	89.10	62.45	26.65
	1,3,5-cyclohexatriene	1.322	1.523			
aug-cc-pVTZ[a]	Benzene	1.392	1.392	80.92	57.81	23.11
	1,3,5-cyclohexatriene	1.324	1.513			

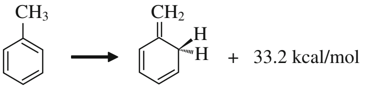
[a] This basis set is less suitable for BLW computations. See text

between benzene and a hypothetical 1,3,5-cyclohexatriene exhibiting *the same amount of conjugation* as in *open* polyenes. The distinction between this hypothetical "conjugated but non-aromatic" 1,3,5-cyclohexatriene and the "optimal" and "rigid" models (both without any π interactions) is clarified in Fig. 2. Although the energy of a hypothetical "conjugated but non-aromatic" 1,3,5-cyclohexatriene cannot be measured experimentally, Kollmar found an easy way to estimate it by noting that the VRE of open polyenes is a linear function of the number of conjugations [48]. This finding has been verified by recent BLW computations [67]. Specifically, Kollmar's VRE estimates of acyclic polyenes were 9.5 kcal/mol (at HF DZ) for 1,3-butadiene, twice as much for linear 1,3,5-hexatriene, and so on, i.e., 9.5 kcal/mol per conjugative interactions between formal double bonds. The ARE of butadiene was calculated to be slightly smaller than the VRE, 9.3 kcal/mol [47]. As there are three conjugative interactions in 1,3,5-cyclohexatriene, the energy of this hypothetical "conjugated but non-aromatic" reference molecule was estimated as the energy of its Kekulé structure lowered by 3 × 9.3 kcal/mol. Equation 10 gives the general relationship between ASE and ARE:

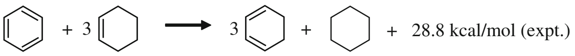
$$\mathrm{ASE} = \mathrm{ARE} - n \times \mathrm{ARE(butadiene)} \quad (10)$$

where n is the number of conjugative interactions in the reference molecule, i.e., 3 in 1,3,5-cyclohexatriene. We will return to this topic below.

Two empirical ASEs evaluations of benzene (Eqs. 11, 12) [27] illustrate recent examples:



(11)



(12)

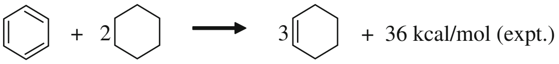
Equation 11 is based on the energy difference between the cyclically delocalized toluene and its merely conjugated isomer, but it suffers from minor group increment, hyperconjugation, and hybridization imbalances and, more significantly, by the presence of only two (rather than three) conjugations in the product. Equation 12 is superior to many other empirical alternatives for several reasons [27]. The three conjugations (see the ASE definition in Eq. 10), the six hyperconjugations, and the strain in the reactants and products balance on both sides of the equation, and there are the same number of bonds of each type, i.e., six π bonds, three $\mathrm{Csp^2}$–$\mathrm{Csp^2}$ bonds, nine $\mathrm{Csp^3}$–$\mathrm{Csp^3}$ bonds, and six $\mathrm{Csp^2}$–$\mathrm{Csp^3}$ bonds. In harmony with Eq. 10, there are three butadiene-like conjugative interactions. Equation 12 has the further conceptual advantage that the butadiene moieties in the reference cyclohexadienes have *syn* conformations (as in benzene) rather than the lower energy anticonformations (favored by acyclic polyenes) [28, 29].

Misleadingly, the 28.8 kcal/mol benzene ASE of Eq. 12 is similar numerically to ZHJVL's 31–32.5 kcal/mol $E_{\mathrm{VRE(VB\text{-}local)}}$ values, but this is only fortuitous. Since such VRE and ASE evaluations are based on completely different concepts (see Fig. 2 and the Discussion below), they are not comparable directly. Similarly, the "historical" 36 kcal/mol RE of Eq. 13 and Fig. 1 [101, 102] has no actual conceptual relationship to ZHJVL's 31–32.5 kcal/mol $E_{\mathrm{VRE(VB\text{-}local)}}$ values.

3 The resonance strength in benzene

Even the most conservative comparison, employing the "historical" empirical RE of 36 kcal/mol (Fig. 1; Eq.13) [101, 102] and the 30 kcal/mol compression energy (ΔE_C) [6, 48, 54, 57, 103], gives a 66 kcal/mol VRE for benzene, close to the early computational value (61.4 kcal/mol) by Norbeck and Gallup [92]. This is two to three times higher than the two sets of VRE values derived by ZHJVL, which range from 20 to 32.5 kcal/mol.

However, even the 66 kcal/mol is considerably underestimated as the value for the benzene VRE. It is based on the highly flawed "historical" empirical RE of benzene deduced from the heat of hydrogenation of cyclohexene (see isodesmic Eq. 13; Fig. 1). This method ignores the strong hyperconjugative stabilization of the three cyclohexene reference molecules. Equation 13 does not compensate for the total of six hyperconjugative methylene group-double bond interactions, worth 5.5 kcal/mol each [50].



(13)

Put simply, Eq. 13 does not measure the RE of benzene properly. As we have stressed repeatedly, *the "historical" 36 kcal/mol resonance stabilization energy of benzene is grossly underestimated* [27, 53]. Equation 13 only measures the difference between the resonance stabilization of benzene (on the left side) and the hyperconjugative stabilization of the three cyclohexene reference molecules (on the right side). When adjusted for this hyperconjugation imbalance, the empirical benzene VRE $= 66 + 5.5 \times 6 = 99$ kcal/mol. ZHJVL's ca. 31 kcal/mol VRE estimates are only about 1/3 as large. In sharp contrast, our pertinent BLW VRE estimates are all near 90 kcal/mol (see Tables 1, 2 as well as the discussion below).

A remarkable advantage of the BLW method is its computational efficiency in geometry optimization and energy calculations, as well as the feasibility of employing both HF and DFT levels [67, 71] by its incorporation into the GAMESS code [115]. The HF and DFT optimized C–C bond lengths, as well as the BLW-computed VRE and ARE values with the 6-31(d), 6-311+G(d,p), cc-pVTZ, and aug-cc-pVTZ basis sets are compared in Tables 1 and 2. Optimizations of the fully delocalized benzene result in slightly shorter CC bonds than given by experiment (1.399 Å), and in general, DFT results are a little better than the HF results, indicating the influence from the electron correlation. For the optimal 1,3,5-cyclohexatriene structure, the CC double bond lengths are essentially the same as in ethene at the same level with the same basis sets, while the single Csp^2–Csp^2 bond lengths, which fluctuate from 1.513 to 1.528 Å, are only slightly shorter than the Csp^3–Csp^3 lengths in ethane. These structural parameters agree with the expectation that the double bonds in the hypothetical 1,3,5-cyclohexatriene should be like those in ethylene and the single Csp^2–Csp^2 bonds should be slightly shorter than the ethane C–C bond. Similar BLW optimizations of linear alkenes result in ca. 1.32 Å double and 1.52 Å single bond lengths consistently, also in accord with the benzene results [53, 54]. Since the BLW VRE values at the HF and DFT levels with the same basis set are very close, the effects of electron correlation and other differences appear to influence both the Kekulé structure and benzene similarly. HF optimizations result in slightly shorter CC bonds than those at DFT ($\sim$0.01 Å with the same basis set). The DFT AREs are about 6 kcal/mol larger than those at the corresponding HF level.

If we consider the aug-cc-pVTZ and larger basis sets not to be suitable for BLW VB RE computations (see the following section), the most reasonable benzene ARE estimates are 62–63 kcal/mol, based on the BLW-DFT results. Note that such values are much higher than the flawed "historical" empirical 36 kcal/mol RE [101, 102] based on Eq. 13 and Fig. 1 (see discussion above) [27, 53]. Although RE is not an experimental observable, its estimation by various methods should converge to reasonably similar results (see Refs. [28, 29, 53]). These should be consistent with accurate experimental and computed data as well as with chemical experience and intuition and should give clear trends and be interpretable for series of similar systems. We believe that the BLW results meet these requirements.

For example, theoretical estimates of the ASE of benzene, deduced from ARE values by means of Eq. 10, can be compared with the ASE = 28.8 kcal/mol derived from the experimental evaluation of Eq. 12. Kollmar's early (1979) ASE evaluation was the forerunner of [close in spirit to] the BLW method, although he used ethylenic π MO's in conjugated systems without further relaxation (polarization). In contrast, all orbitals in BLW are optimized self-consistently. Kollmar's computed VRE and

ARE of *anti*-1,3-butadiene with a DZ basis set were nearly the same, 9.5 and 9.3 kcal/mol [48], but the corresponding benzene VRE = 96.4 and ARE = 56.0 kcal/mol differed by 40.4 kcal/mol (the compression energy, ΔE_C, in Eq. 9). Kollmar concluded that the "normalized resonance energies [i.e., ASE] we obtain for benzene were 28 kcal/mol with SCF and 26 kcal/mol with inclusion of correlation". These values, which were obtained from a purely theoretical calculation, compare surprisingly well with thermochemical estimations [cf., e.g., the ASE = 28.8 kcal/mol of Eq. 10]. Our results for the comparable HF BLW calculations (VRE ~90, ARE ~56, and ΔE_C ~34 kcal/mol, Table 1, first two entries) corroborate Kollmar's remarkably well. To evaluate the benzene ASE, we use Eq. 10 and the BLW AREs. For this purpose, the *syn*-1,3-butadiene conformer (ARE's 8.8 and 10.0 kcal/mol at HF/6-31G(d) and HF/6-311+G(d), respectively) is more suitable conceptually than the *anti* conformer (but the latter has only slightly larger AREs). The resulting ASE values, 28.7 and 27.5 kcal/mol at HF/6-31G(d) and HF/6-311+G(d), respectively, are in close agreement with the best experimental estimation, 28.8 kcal/mol, Eq. 12, as well as Kollmar's 28 kcal/mol.

The BLW ARE for benzene agrees remarkably well with a recent comprehensive empirical assessment [28, 29], including the isodesmic evaluation, $3\ C_2H_6 + 3\ C_2H_4 \rightarrow C_6H_6 + 6\ CH_4$, which gives ARE = 65.5 kcal/mol. The latter is based on the earliest definition of RE by Hückel as the energy difference between the π MO's in a conjugated system and those in ethylene [1, 2]. Note, however, that the hypothetical 1,3,5-cyclohexatriene Kekulé structure implied by the equation has double bonds based on ethylene but single bonds based on ethane even though the carbon atoms of the later are sp^3 rather than sp^2 hybridized.

4 The basis set artifact

VB theory and its concepts were based essentially on chemical intuition, in particular that molecules are composed of individual fragments. But in this ab initio era, how can these conceptual ideas be described mathematically? How should atomic orbitals be represented? STOs derived from the exact solution of the Schrödinger equation for the hydrogen atom are the best candidates. The linear combination of atomic orbitals is the straightforward way to construct MOs and VB functions. Unfortunately, the computational obstacle of evaluating four-index integrals is yet to be overcome. In 1950, Boys introduced the Gaussian functions where the radial decays of the original STOs change from e^{-r} to e^{-r^2} [116]. While the dramatic reduction in computational costs using GTOs revolutionized computational chemistry, the variational principle drives the continuing development of large toward complete basis sets. On one hand, this is essential for the examination of quantum laws and the ultimate comparisons with subtle experiments. But on the other hand, the departure from the atomic concepts with extremely large basis sets diminishes the advantages of VB theory versus MO theory. The completeness of basis sets diffuses the familiarized picture by chemists that molecules are composed of atoms or functional groups and imposes challenge how to interpret computational results in a physically intuitive way. Mulliken clearly realized this dilemma in the beginning of MO theory and insightfully pointed out that "the more accurate the calculations become, the more the concepts tend to vanish into thin air" [117].

MO theory builds the wavefunction for a molecular state with delocalized MOs, which are linear combinations of all basis functions. Thus, the completeness of basis sets leads to low molecular energy according to the variational principle and approaches the "real" state from the exact solution of the Schrödinger equation. VB theory adopts an alternative philosophy and builds the wavefunction for a molecular state with a set of electron-localized Lewis resonance structures. The completeness of basis sets similarly leads to low molecular energy, as ultimately MO and VB theories are equivalent. However, large basis sets tend to blur the boundary among resonance structures where electron pairs are localized to bonds and atoms. If we follow the original Pauling–Wheland definition, RE computations necessarily will run into a "basis set artifact." We disagree with ZHJVL's discussion based on a difference between VB and BLW. BLW is the most simplified variant of VB theory (see Sect. 1), rather than being distinctly different. All VB as well as BLW computations of REs eventually will encounter such "basis set artifacts". However, this is not a major problem in practice for most chemical systems, as infinite basis sets are not practicable except for small molecules. As we have demonstrated [54, 69–71] and show again in Tables 1 and 2, widely available medium-size basis sets (small enough to keep the local character of optimized AOs but large enough to provide accurate molecular properties) are the best choices for VB applications that require the definition of reference structures having a desired bonding scheme (like 1,3,5-cyclohexatriene).

Modern quantum chemistry accepts the fact that various practicable theoretical levels give numerical results that do not agree precisely. Pople's "model chemistries" [115] emphasized the desirability of basing interpretations on comparisons of data obtained at uniform theoretical levels, since errors tend to cancel. In actual fact, computed BLW values vary only modestly in typical applications with the size of usually employed basis sets or between HF and DFT. We agree with ZHJVL that the important concept of “resonance energy” is used by different authors with different meanings, resulting in confusion. We hope that the present paper clarifies the simple distinctions among the vertical resonance energy (VRE), the adiabatic resonance energy (ARE), and the aromatic stabilization energy (ASE) by showing how these different quantities are related. The ASE is most closely related to what chemists actually regard as being the “special character” of benzene, which influences their experiments. While BLW VRE and ARE computations agree with empirical evaluations, the VB-deloc and VB-local approaches adopted by ZHJVL give VRE values that are far too small.

ZHJVL employed computations on hypothetical H_6 to illustrate the relatively large basis set dependency of the BLW RE estimates. Although the VB-deloc and VB-local methods did not have this dependency, we note that these computational RE approaches have other fundamental imperfections, as noted above. Also, no comparisons with experiment are possible. ZHJVL’s hexagonal H_6 with fixed 0.74 Å bond lengths seems unduly compressed, when the aromatic D_{6h} H_6 transition structure has ca. 0.99 Å HH distances and at least a semblance of reality.

However, our extensive studies (see, e.g., Tables 1, 2) clearly demonstrated that the BLW method, when used with mid-size basis sets (such as cc-pVTZ) can generate reasonably level-invariant REs which are consistent with the evidence of experimental and MO evaluations.

5 Conclusions

We argue that ZHJVL’s [58] approaches to derive Pauling-Wheland resonance energies (RE) within VB theory are inappropriate since their definition of RE does not lead to results consistent with those based on experimental data. According to Pauling–Wheland, RE is the energy difference between the real conjugated (delocalized) system and the corresponding most stable virtual resonance structure (localized). Consequently, it is essential to construct the wavefunctions for both delocalized and localized states at the same theoretical level. Moreover, the definition of the localized state should closely correspond to the intuitive picture of the corresponding VB structure. But the ZHJVL approaches used partially delocalized wave functions for the localized states in their VB-delocal approach, or wave functions lacking the ionic components in their VB-local method. In both cases, applications result in severely underestimated RE’s when compared to available experimental data. In contrast, the simplest variant of ab initio VB theory, the BLW method, when employed with mid-sized basis sets, generates reasonably level-invariant RE values consistent with the best evaluations based on experimental data and MO-based computations. The consistency between theoretical determinations of REs and evaluations based on experimental data is essential, in our view, in order to validate the reliability of RE computations for the prediction of the energetic stabilities of new molecules.

VB theory describes molecules in terms of electron-localized resonance structures. However, boundaries among resonance structures are blurred when large basis sets approaching completeness are employed. Hence, RE computations within any variation of VB theory necessarily may run into this “basis set artifact” problem. However, our extensive BLW computations demonstrated that mid-size basis sets can generate satisfactory results, whose considerable interpretative advantages far outweigh the insignificant technical disadvantages. Hence, we expect that ab initio VB studies will continue to thrive and provide insightful and unique information on the nature of molecular bonding, complementary to those from MO computations.

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References

1. Hückel E (1931) Z Physik 71:204
2. Hückel E (1932) Z Physik 76:628
3. Pauling L (1967) The chemical bond, 1st edn. Cornell University Press, Ithaca
4. Pauling LC, Wheland GW (1933) J Chem Phys 1:362
5. Wheland GW (1944) The theory of resonance. Wiley, New York, p 52
6. Wheland GW (1955) Resonance in organic chemistry. Wiley, New York
7. Schleyer PvR (2001) Chem Rev 101:1115
8. Bird CW (1985) Tetrahedron 41:1409
9. Garratt PJ (1986) Aromaticity, 3rd edn. Wiley, New York
10. Jug K, Koster AM (1991) J Phys Org Chem 4:163
11. Schleyer PvR, Maerker C, Dransfeld A, Jiao H, van Eikema Hommes NJR (1996) J Am Chem Soc 118:6317
12. Bird CW (1997) Tetrahedron 53:3319
13. Chesnut DB (2000) Chem Phys 231:1
14. Abraham RJ, Canton M, Reid M, Griffiths LJ (2000) Chem Soc Perkin Trans 2:803
15. Krygowski TM, Cyrański MK, Czarnocki Z, Hafelinger G, Katritzky AR (2000) Tetrahedron 56:1783
16. Cyrański MK, Krygowski TM, Katritzky AR, Schleyer PvR (2002) J Org Chem 67:1333
17. Tsipis CA, Karagiannis EE, Kladou PF, Tsipis AC (2004) J Am Chem Soc 126:12916
18. Mills NS, Levy A, Plummer BF (2004) J Org Chem 69:6623
19. Poater J, García-Cruz I, Illas F, Solà M (2004) Phys Chem Chem Phys 6:314
20. Lazzeretti P (2004) Phys Chem Chem Phys 6:217
21. Matito E, Duran M, Sola M (2005) J Chem Phys 122, Art. No. 014109

22. Minkin VI, Glukhovtsev MN, Simkin BY (1994) Aromaticity and antiaromaticity: electronic and structural aspects. Wiley, New York
23. Cooper DL (ed) (2002) Valence bond theory. Elsevier, Amsterdam
24. Gallup GA (2002) Valence bond methods: theory and applications. Cambridge University Press, New York
25. Shaik SS, Hiberty PC (2008) A chemist's guide to valence bond theory. Wiley, Hoboken
26. Dewar MJS, Schmeising HN (1959) Tetrahedron 5:166
27. Schleyer PvR, Puhlhofer F (2002) Org Lett 4:2873
28. Wodrich MD, Wannere CS, Mo Y, Jarowski PD, Houk KN, Schleyer PvR (2007) Chem Eur J 13:7731
29. Kemnitz CR, Mackey JL, Loewen ML, Hargrove JL, Lewis JL, Hawkins WE, Nielsen AF (2010) Chem Eur J 16:4942
30. van Dranen J, Ketelaar JAA (1950) J Chem Phys 18:151
31. Hornig DF (1950) J Am Chem Soc 72:5772
32. Glockler G (1953) J Chem Phys 21:1249
33. Streitwieser A (1961) Molecular orbital theory for organic chemists. Wiley, New York and references therein
34. Hess BA Jr, Schaad LJ (1983) J Am Chem Soc 105:7500
35. George P, Bock CW, Trachtman M (1985) Tetrahedron Lett 26:5667
36. Janoschek R (1991) J Mol Struct (THEOCHEM) 229:197
37. Collins JR, Gallup GA (1991) THEOCHEM 75:91
38. Matsunaga N, Cundari TR, Schmidt MW, Gordon MS (1992) Theor Chim Acta 83:57
39. Tao FM, Pan YK (1992) Theor Chim Acta 83:377
40. Glendening ED, Faust R, Streitwieser A, Vollhardt KPC, Weinhold F (1993) J Am Chem Soc 115:10952
41. Behrens S, Koster AM, Jug K, Koster AM (1994) J Org Chem 59:2546
42. Exner O, Bohm S (2000) J Chem Soc Perkin Trans 2:1994
43. Schaad LJ, Hess BA (2001) Chem Rev 101:1465
44. Suresh CH, Koga N (2002) J Org Chem 67:1965
45. Chen Z, Song J, Song L, Wu W (2008) J Theoret Comput Chem 7:655
46. Dewar MJS, De Llano C (1969) J Am Chem Soc 91:789
47. Tantardini GF, Raimondi M, Simonetta M (1977) J Am Chem Soc 99:2913
48. Kollmar H (1979) J Am Chem Soc 101:4832
49. Cooper DL, Gerratt J, Raimondi M (1986) Nature 323:699
50. Shaik SS, Hiberty PC, Lefour JM, Ohanessian G (1987) J Am Chem Soc 109:363
51. Mo Y, Wu W, Zhang Q (1994) J Phys Chem 98:10048
52. van Lenthe JH, Havenith RWA, Dijkstra F, Jenneskens LW (2002) Chem Phys Lett 361:203
53. Mo Y, Schleyer PvR (2006) Chem Eur J 12:2009
54. Mo Y (2009) J Phys Chem A 113:5163
55. Mulliken RS, Rieke CA, Brown WG (1941) J Am Chem Soc 63:41
56. Jug K, Hiberty PC, Shaik S (2001) Chem Rev 101:1477
57. Mulliken RS, Parr RG (1951) J Chem Phys 19:1271
58. Zielinski M, Havenith RWA, Jenneskens LW, van Lenthe JH (2010) Theor Chem Acc. doi:10.1007/s00214-010-0793-8
59. Dijkstra F, van Lenthe JH, Havenith RWA, Jenneskens LW (2003) Int J Quantum Chem 91:566
60. Zielinski M, van Lenthe JH (2008) J Phys Chem A 112:13197
61. van Lenthe JH, Balint-Kurti GG (1980) Chem Phys Lett 76:138
62. van Lenthe JH, Balint-Kurti GG (1983) Chem Phys 76:5699
63. Hiberty PC (1997) THEOCHEM 398–399:35
64. Hiberty PC, Flament JP, Noizet E (1992) Chem Phys Lett 189:259
65. Hiberty PC, Humbel S, Byrman CP, van Lenthe JH (1994) J Chem Phys 101:5969
66. Hiberty PC, Shaik S (2002) Theor Chem Acc 108:255
67. Mo Y (2003) J Chem Phys 119:1300
68. Mo Y (2004) J Org Chem 69:5563
69. Mo Y, Gao J, Peyerimhoff SD (2000) J Chem Phys 112:5530
70. Mo Y, Peyerimhoff SD (1998) J Chem Phys 109:1687
71. Mo Y, Song L, Lin Y (2007) J Phys Chem A 111:8291
72. Kerber RC (2006) J Chem Edu 83:223
73. Pauncz R (1979) Spin eigenfunctions—construction and use. Plenum Press, New York
74. McWeeny R (1989) Methods of molecular quantum mechanics, 2nd edn. Academic, London
75. Gallup GA, Vance RL, Collins JR, Norbeck JM (1982) Adv Quant Chem 16:229
76. Zhang Q, Li X (1989) J Mol Struct 189:413
77. Thorsteinsson T, Cooper DL (1998) J Math Chem 23:105
78. Wu W, Wu A, Mo Y, Lin M, Zhang Q (1998) Int J Quantum Chem 67:287
79. Mcweeny R (1999) Int J Quantum Chem 74:87
80. Shaik S, Shurki A (1999) Angew Chem Int Ed 38:586
81. Raimondi M, Cooper DL (1999) Top Curr Chem 203:105
82. Dijkstra F, van Lenthe JH (2000) J Chem Phys 113:2100
83. Wu W, Song L, Mo Y, Zhang Q (2000) XIAMEN—an ab initio spin-free valence bond (VB) program. Xiamen University, Xiamen
84. Song L, Mo Y, Zhang Q, Wu W (2005) J Comput Chem 26:514
85. Cooper DL, Gerratt J, Raimondi M (1991) Chem Rev 91:929
86. Slater JC (1931) Phys Rev 38:110
87. Mo Y, Gao J (2007) Acc Chem Res 40:113
88. Mo Y, Wu W, Song L, Lin M, Zhang Q, Gao J (2004) Angew Chem Int Ed 43:1986
89. Payne PW, Allen LC (1977) In Schaefer III HF (ed) Modern theoretical chemistry. Plenum Press, New York, vol 4, pp 29
90. Wiberg KB (1998) In: Schelyer PvR (ed) Encyclopedia of computational chemistry. Wiley, Berlin, p 2518
91. Mo Y (2010) Nat Chem 2:666
92. Norbeck JM, Gallup GA (1974) J Am Chem Soc 96:3386
93. Hiberty PC, Ohanessian G (1985) Int J Quantum Chem 27:245
94. Hiberty PC, Ohanessian G (1985) Int J Quantum Chem 27:259
95. Bobrowicz FW, Goddard WA III (1977) In: Schaefer HF III (ed) Methods of electronic structure theory. Plenum, New York, p 79
96. Coulson CA, Fischer I (1949) Phil Mag 40:306
97. Mueller CR, Eyring H (1951) J Chem Phys 19:1495
98. Mo Y, Lin Z, Wu W, Zhang Q (1996) J Phys Chem 100:11569
99. Hiberty PC, Byrman CP (1995) J Am Chem Soc 117:9875
100. Lauvergnat D, Hiberty PC (1997) J Am Chem Soc 119:9478
101. Kistiakowsky GB, Romeyn H Jr, Ruhoff JR, Smith HA, Vaughan WE (1936) J Am Chem Soc 57:65
102. Kistiakowsky GB, Ruhoff JR, Smith HA, Vaughan WE (1936) J Am Chem Soc 58:137
103. Coulson CA, Altmann SL (1952) Trans Faraday Soc 48:293
104. Shaik SS, Hiberty PC, Ohanessian G, Lefour JM (1988) J Phys Chem 92:5086
105. Shaik S, Shurki A, Danovich D, Hiberty PC (2001) Chem Rev 101:1501
106. Wu JI, Dobrowolski MA, Cyrański MK, Merner BL, Bodwell GJ, Mo Y, Schleyer PvR (2009) Mol Phys 107:1177
107. Pauling L, Sherman J (1936) J Chem Phys 1:606
108. Exner K, Schleyer PvR (2001) J Phys Chem A 105:3407
109. George P, Trachtman M, Bock CW, Brett AM (1975) Tetrahedron 38:121
110. George P, Trachtman M, Bock CW, Brett AM (1976) Tetrahedron 32:317
111. Hehre WJ, Radom L, Schleyer PvR, Pople JA (1986) Ab initio molecular orbital theory. Wiley, New York
112. Slayden SW, Liebman JF (2001) Chem Rev 101:1541

113. Cyrański MK, Schleyer PvR, Krygowski TM, Jiao H, Hohlneicher G (2003) Tetrahedron 59:1657
114. Cyrański MK (2005) Chem Rev 105:3773
115. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JJ, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JAJ (1993) J Comput Chem 14:1347
116. Boys SF (1950) Proc R Soc Lond A 200:542
117. Mulliken RS (1965) J Chem Phys 43:S2