Electronic Supplementary Information

A Reliable and Efficient Resonance Theory Based on Analysis of DFT Wave Functions

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1 Total Number of Possible Lewis Structures

In an N_cc-N_ee closed-shell system, for all Lewis structures with a fixed number of lone pairs, λ, the number of different ways of assigning the $N_\mathrm{e}/2$ electron pairs can be counted as follows. First, we pick up λ out of the N_c atoms to accommodate λ lone pairs, which has the number of possibilities being

$$N_1^\lambda = C_{N_\mathrm{c}}^\lambda = \frac{N_\mathrm{c}!}{\lambda!\,(N_\mathrm{c}-\lambda)!} \tag{S1}$$

Second, we choose 2 atoms out of the remaining $(N_\mathrm{c}-\lambda)$ ones to form a covalent bond, giving rise to $C_{N_\mathrm{c}-\lambda}^2$ choices. Subsequently, we choose another 2 out of $(N_\mathrm{c}-\lambda-2)$ atoms for the next covalent bond, resulting in $C_{N_\mathrm{c}-\lambda-2}^2$ choices, $\ldots$, and so on. By continuing the above procedure until all electron pairs have been run out, we end up with the number of all possible combinations for the whole second step as

$$\begin{aligned} N_2^\lambda &= C_{N_\mathrm{c}-\lambda}^2 \cdot C_{N_\mathrm{c}-\lambda-2}^2 \cdots C_{N_\mathrm{c}-\lambda-2(N_\mathrm{e}/2-\lambda)}^2 / (N_\mathrm{e}/2-\lambda)! \\ &= \frac{(N_\mathrm{c}-\lambda)!}{2^{N_\mathrm{e}/2-\lambda}\,(N_\mathrm{c}+\lambda-N_\mathrm{e})!\,(N_\mathrm{e}/2-\lambda)!} \end{aligned} \tag{S2}$$

Note that the presence of the term $(N_\mathrm{e}/2-\lambda)!$ in the denominator is because we do not distinguish the order of successive steps of choosing 2 atoms. Thus, the total number of Lewis structures with λ lone pairs is

$$N_\mathrm{Lewis}^\lambda = N_1^\lambda N_2^\lambda = \frac{N_\mathrm{c}!}{\lambda!\,(N_\mathrm{c}+\lambda-N_\mathrm{e})!\,(N_\mathrm{e}/2-\lambda)!\,2^{N_\mathrm{e}/2-\lambda}} \tag{S3}$$

Hence, the total number of all possible Lewis structures is given by

$$N_\mathrm{Lewis} = \sum_{\lambda=0}^{N_\mathrm{e}/2} N_\mathrm{Lewis}^\lambda = \sum_{\lambda=0}^{N_\mathrm{e}/2} \frac{N_\mathrm{c}!}{\lambda!\,(N_\mathrm{c}+\lambda-N_\mathrm{e})!\,(N_\mathrm{e}/2-\lambda)!\,2^{N_\mathrm{e}/2-\lambda}} \tag{S4}$$

2 The VB Description of Lewis Structure Wave Functions Is Equivalent to the LSD Description

For a lone pair on atom A, the VB description and that in this work are obviously identical, i.e., the wave function is expressed as a single determinant in terms of a 1c-LUO, ϕ_A:

$$\Phi_A = \Phi_A^{\mathrm{VB}} = |\phi_A\overline{\phi}_A| = |\varphi_A\overline{\varphi}_A| \tag{S5}$$

where φ_A is the effective atomic orbital of A. The two definitions differ in the wave function of a pure covalent bond between atoms A and B. In the VB theory, a Heitler–London function is utilized, and its normalized form is written as

$$\Phi_{AB}^{\mathrm{HL}} = \frac{1}{\sqrt{2}}\big(|\varphi_A\overline{\varphi}_B| - |\overline{\varphi}_A\varphi_B|\big) \tag{S6}$$

Note that it is presumed here that an orthonormal atomic basis set is used and therefore $\langle\varphi_A|\varphi_B\rangle = 0$. The LSD description of a pure covalent bond uses a single determinant in terms of a 2c-LUO, ϕ_{AB}:

$$\Phi_{AB} = |\phi_{AB}\overline{\phi}_{AB}| = \left|\frac{1}{\sqrt{2}}(\varphi_A+\varphi_B)\overline{\frac{1}{\sqrt{2}}(\varphi_A+\varphi_B)}\right| \tag{S7}$$

Using Moffitt's theorem,[1–3] we can expand eq S7 as

$$\Phi_{AB} = \frac{1}{2}\big(|\varphi_A\overline{\varphi}_B| - |\overline{\varphi}_A\varphi_B| + |\varphi_A\overline{\varphi}_A| + |\varphi_B\overline{\varphi}_B|\big) \tag{S8}$$

Comparing eq S8 with eqs S6 and S5, we know that

$$\Phi_{AB} = \frac{1}{\sqrt{2}}\Phi_{AB}^{\mathrm{HL}} + \frac{1}{2}(\Phi_A + \Phi_B) \tag{S9}$$

This equation gives the linear relationship between the LUO Φ_{AB} and the Heitler–London function Φ_{AB}^{HL}. Therefore, any VB wave function of a molecular system can be equivalently transformed into the wave function in terms of the LUOs, and *vice versa*.

Taking a diatomic molecule, A—B, as an example, we can describe the σ bond using a wave function in terms of 1c- and 2c-LUOs, as

$$\Psi_{AB} = \lambda\Phi_{AB} + \mu(\Phi_A + \Phi_B) \tag{S10}$$

where λ and μ are the coefficients for the covalent and ionic Lewis structures, respectively, for describing the actual A—B bond. Alternatively, the wave function of this bond can also be expressed by a VB wave function:[4]

$$\Psi_{AB} = \tilde{\lambda}\Phi_{AB}^{\mathrm{HL}} + \tilde{\mu}(\Phi_A + \Phi_B) \tag{S11}$$

Plugging eq S9 into eq S10 and then comparing with eq S11, we obtain

$$\tilde{\lambda} = \frac{\lambda}{\sqrt{2}}; \quad \tilde{\mu} = \mu + \frac{\lambda}{2} \tag{S12}$$

and

$$\lambda = \sqrt{2}\tilde{\lambda}; \quad \mu = \tilde{\mu} - \frac{\lambda}{2} \tag{S13}$$

For a homonuclear bond like in the H_2 molecule, $\lambda = 1, \mu = 0$, then $\tilde{\lambda} = \frac{1}{\sqrt{2}}, \tilde{\mu} = \frac{1}{2}$:

$$\Psi_{AB}(\mathrm{H}_2) = \Phi_{AB} = \frac{1}{\sqrt{2}}\Phi_{AB}^{\mathrm{HL}} + \frac{1}{2}(\Phi_A + \Phi_B) \tag{S14}$$

3 Overlap and Hamiltonian Matrices between LSDs

3.1 Overlap matrix

For an open-shell system with m α electrons and n β electrons ($m \geqslant n$), the LSD of the i-th Lewis structure is expressed as

$$\Psi_i = |\phi_{i1}\phi_{i2}\cdots\phi_{im}\overline{\phi}_{i1}\overline{\phi}_{i2}\cdots\overline{\phi}_{in}| \tag{S15}$$

where $\{\phi_{ik}\}$ and $\{\overline{\phi}_{il}\}$ are, respectively, the α and β LUOs ($k = 1, 2, \cdots, m$ and $l = 1, 2, \cdots, n$). Note that, in a spin-unrestricted scheme, the α-LUO ϕ_{ik} and β-LUO $\overline{\phi}_{jk}$ corresponding to the same lone pair or covalent bond are not necessarily the same spatial orbitals. According to Löwdin's result,[5,6] the overlap between two LSDs is given by the following determinant:

$$S_{ij} = \langle\Psi_i|\Psi_j\rangle = \begin{vmatrix} \mathbf{S}_{ij}^{\alpha\alpha} & \mathbf{S}_{ij}^{\alpha\beta} \\ \mathbf{S}_{ij}^{\beta\alpha} & \mathbf{S}_{ij}^{\beta\beta} \end{vmatrix} \tag{S16}$$

where the sub-determinants $|\mathbf{S}_{ij}^{\alpha\alpha}|$, $|\mathbf{S}_{ij}^{\alpha\beta}|$, $|\mathbf{S}_{ij}^{\beta\alpha}|$ and $|\mathbf{S}_{ij}^{\beta\beta}|$ are

$$\begin{aligned} |\mathbf{S}_{ij}^{\alpha\alpha}| &= |\langle\phi_{ik}|\phi_{jl}\rangle|; \qquad & |\mathbf{S}_{ij}^{\alpha\beta}| &= |\langle\phi_{ik}|\overline{\phi}_{jl}\rangle|; \\ |\mathbf{S}_{ij}^{\beta\alpha}| &= |\langle\overline{\phi}_{ik}|\phi_{jl}\rangle|; \qquad & |\mathbf{S}_{ij}^{\beta\beta}| &= |\langle\overline{\phi}_{ik}|\overline{\phi}_{jl}\rangle|. \end{aligned} \tag{S17}$$

Since the α and β spin wave functions are orthogonal to each other, $|\mathbf{S}_{ij}^{\alpha\beta}| = |\mathbf{S}_{ij}^{\beta\alpha}| = 0$. Hence, the determinant in eq S16 is block diagonal and therefore

$$S_{ij} = |\mathbf{S}_{ij}^{\alpha\alpha}| \cdot |\mathbf{S}_{ij}^{\alpha\alpha}| = |\langle\phi_{ik}|\phi_{jl}\rangle| \cdot |\langle\overline{\phi}_{ik}|\overline{\phi}_{jl}\rangle| \equiv S_{ij}^{\alpha} \cdot S_{ij}^{\beta} \tag{S18}$$

For a closed-shell system as a special case, the overlap matrix of LSDs is

$$S_{ij} = \left(S_{ij}^{\alpha}\right)^2 = |\langle\phi_{ik}|\phi_{jl}\rangle|^2 \qquad (k, l = 1, 2, \ldots, m) \tag{S19}$$

3.2 Hamiltonian matrix

For an open-shell system, using Löwdin's result,[5,6] the Hamiltonian matrix of LSDs is

$$H_{ij} = \langle\Psi_i|\hat{h}|\Psi_j\rangle = \sum_{r=1}^{m} \begin{vmatrix} \mathbf{H}_{ij}^{r,\alpha\alpha} & \mathbf{H}_{ij}^{r,\alpha\beta} \\ \mathbf{S}_{ij}^{\beta\alpha} & \mathbf{S}_{ij}^{\beta\beta} \end{vmatrix} + \sum_{r=1}^{n} \begin{vmatrix} \mathbf{S}_{ij}^{\alpha\alpha} & \mathbf{S}_{ij}^{\alpha\beta} \\ \mathbf{H}_{ij}^{r,\beta\alpha} & \mathbf{H}_{ij}^{r,\beta\beta} \end{vmatrix} \tag{S20}$$

where the sub-determinant $\left|\mathbf{H}_{ij}^{r,\alpha\alpha}\right|$, $\left|\mathbf{H}_{ij}^{r,\alpha\beta}\right|$, $\left|\mathbf{H}_{ij}^{r,\beta\alpha}\right|$ and $\left|\mathbf{H}_{ij}^{r,\beta\beta}\right|$ are

$$\left|\mathbf{H}_{ij}^{r,\alpha\alpha}\right| = \left|\langle\phi_{ik}|\hat{h}_r|\phi_{jl}\rangle\right|; \qquad \left|\mathbf{H}_{ij}^{r,\alpha\beta}\right| = \left|\langle\phi_{ik}|\hat{h}_r|\overline{\phi}_{jl}\rangle\right|; \tag{S21}$$

$$\left|\mathbf{H}_{ij}^{r,\beta\alpha}\right| = \left|\langle\overline{\phi}_{ik}|\hat{h}_r|\phi_{jl}\rangle\right|; \qquad \left|\mathbf{H}_{ij}^{r,\beta\beta}\right| = \left|\langle\overline{\phi}_{ik}|\hat{h}_r|\overline{\phi}_{jl}\rangle\right|, \tag{S22}$$

in which $\hat{h}_r$ equals the one-electron Kohn–Sham (Fock) operator, $\hat{h}$, if $k = r$ and otherwise the identity operator, $\hat{1}$. Noticing that $\left|\mathbf{H}_{ij}^{r,\alpha\beta}\right| = \left|\mathbf{H}_{ij}^{r,\beta\alpha}\right| = 0$ because of the orthogonality between different spins, we have

$$H_{ij} = \sum_{r=1}^{m} \left|\mathbf{H}_{ij}^{r,\alpha\alpha}\right| \cdot \left|\mathbf{S}_{ij}^{\beta\beta}\right| + \sum_{r=1}^{n} \left|\mathbf{S}_{ij}^{\alpha\alpha}\right| \cdot \left|\mathbf{H}_{ij}^{r,\beta\beta}\right| \tag{S23}$$

$$= \left|\langle\overline{\phi}_{ik}|\overline{\phi}_{jl}\rangle\right| \sum_{r=1}^{m} \left|\langle\phi_{ik}|\hat{h}_r|\phi_{jl}\rangle\right| \; + \; \left|\langle\phi_{ik}|\phi_{jl}\rangle\right| \sum_{r=1}^{n} \left|\langle\overline{\phi}_{ik}|\hat{h}_r|\overline{\phi}_{jl}\rangle\right|$$

$$\equiv S_{ij}^{\beta} \sum_{r}^{\alpha-\text{LUOs}} H_{ij}^{r,\alpha} \; + \; S_{ij}^{\alpha} \sum_{r}^{\beta-\text{LUOs}} H_{ij}^{r,\beta} \tag{S24}$$

where $k = 1, 2, \ldots, m$ and $l = 1, 2, \ldots, n$.

Evidently, for a closed-shell system, $S_{ij}^{\alpha} = S_{ij}^{\beta} = \sqrt{S_{ij}}$ (cf. eq S19) and $H_{ij}^{r,\alpha} = H_{ij}^{r,\beta} \equiv H_{ij}^{r}$, so the Hamiltonian matrix of LSDs is

$$H_{ij} = 2\sqrt{S_{ij}} \sum_{r=1}^{m} H_{ij}^{r} \tag{S25}$$

3.3 Energies of Lewis structures

Let us define the energy of the i-th Lewis structure as the expectation value of the Hamiltonian operator on the wave function of that Lewis structure. Accordingly, it is given by the corresponding diagonal entry of the Hamiltonian matrix of LSDs, i.e.

$$E_i \equiv \langle\Psi_i|\hat{H}|\Psi_i\rangle = H_{ii} \tag{S26}$$

Using eq S24 and noticing that $S_{ii}^{\alpha} = S_{ii}^{\beta} = 1$, we have

$$E_i = H_{ii} = \sum_{r}^{\alpha-\text{LUOs}} H_{ii}^{r,\alpha} \; + \; \sum_{r}^{\beta-\text{LUOs}} H_{ii}^{r,\beta} = \sum_{r=1}^{m} \left|\langle\phi_{ik}|\hat{h}_r|\phi_{il}\rangle\right| \; + \; \sum_{r=1}^{n} \left|\langle\overline{\phi}_{ik}|\hat{h}_r|\overline{\phi}_{il}\rangle\right| \tag{S27}$$

It is noticed that the two different LUOs ϕ_{ik} and ϕ_{il} (for $k \neq l$) present in the same Lewis structure are composed of distinct RAOs, because each RAO is exclusively assigned to one lone pair or one bond. As the RAOs are mutually orthogonal, ϕ_{ik} and ϕ_{il} are orthogonal to each other as well. This means that all off-diagonal entries of determinant $H_{ii}^{r,\alpha}$ are zero except in the r-th row (see eq S24). Thus,

$$H_{ii}^{r,\alpha} = \langle \phi_{ir} | \hat{h} | \phi_{ir} \rangle \equiv \varepsilon_{ir}^{\alpha} \tag{S28}$$

As we can see, the meaning of $H_{ii}^{r,\alpha}$ is the energy of the α-LUO ϕ_{ir}, denoted by $\varepsilon_{ir}^{\alpha}$. Likewise, $H_{ii}^{r,\beta} = \langle \overline{\phi}_{ir} | \hat{h} | \overline{\phi}_{ir} \rangle = \varepsilon_{ir}^{\beta}$, which is the energy of the β-LUO $\overline{\phi}_{ir}$. Therefore, from eq S27, we obtain the energy of the i-th Lewis structure as

$$E_i = H_{ii} = \sum_{r=1}^{m} \varepsilon_{ir}^{\alpha} + \sum_{r=1}^{n} \varepsilon_{ir}^{\beta} = \sum_{r}^{\text{All LUOs}} \varepsilon_{ir} \tag{S29}$$

where ε_{ir} denotes the energy of any individual LUO irrespective of the spin.

For a closed-shell system, each LUO is doubly occupied, and hence the energy of a Lewis structure is

$$E_i = H_{ii} = 2 \sum_{r=1}^{m} \varepsilon_{ir} \tag{S30}$$

3.4 Interaction energies between Lewis structures

By using the expansion of Ψ (eq 1 in the main text), the reference energy of the resonance hybrid is

$$E \equiv \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i} c_i^2 H_{ii} + \sum_{i} \sum_{j \neq i} c_i^* c_j H_{ij} = \sum_{i} c_i^2 E_i + \sum_{i} \sum_{j \neq i} c_i^* c_j H_{ij} \tag{S31}$$

Meanwhile, from the Chirgwin–Coulson weight w_i,[7] we have

$$c_i^2 = w_i - \sum_{j \neq i} c_i^* c_j S_{ij} \tag{S32}$$

Plugging eq S32 into S31, we obtain

$$E = \sum_{i} w_i E_i + \sum_{i} \sum_{j \neq i} c_i^* c_j \big(H_{ij} - E_i S_{ij} \big) \tag{S33}$$

3.5 Overlap and Hamiltonian integrals between two Lewis structures depend only on the distinct bonds/lone pairs

Let us consider in a closed-shell system two Lewis structures sharing some common bonds and/or lone pairs. Suppose two LSDs, Ψ_i and Ψ_j, have h LUOs in common, i.e.,

$$\begin{aligned}\Psi_i &= |\phi_1\overline{\phi}_1\phi_2\overline{\phi}_2\cdots\phi_h\overline{\phi}_h\,\phi_{i1}\overline{\phi}_{i1}\phi_{i2}\overline{\phi}_{i2}\cdots\phi_{ig}\overline{\phi}_{ig}| \\ \Psi_j &= |\phi_1\overline{\phi}_1\phi_2\overline{\phi}_2\cdots\phi_h\overline{\phi}_h\,\phi_{j1}\overline{\phi}_{j1}\phi_{j2}\overline{\phi}_{j2}\cdots\phi_{jg}\overline{\phi}_{jg}|\end{aligned} \tag{S34}$$

It is follows that all LUOs within an LSD are orthogonal to each other since none of them share the same RAOs and the RAOs form an orthogonal set. As a result, any two LUOs appeared in Ψ_i and Ψ_j, regardless of the spin, are orthogonal to each other, except for those from the distinct set of LUOs, i.e., ϕ_{ik} and ϕ_{jk} $(k = 1, 2, \ldots, g)$. Consequently, using eq S16 and the property of a block triangular determinant, we obtain

$$S_{ij} = S_{ij}^{\text{comm}} \cdot S_{ij}^{\text{diff}} \tag{S35}$$

where S_{ij}^{comm} is the determinant of overlap integrals between the common set of LUOs, i.e., $\{\phi_k, \overline{\phi}_k\}$ $(k = 1, 2, \ldots, h)$; S_{ij}^{diff} is the determinant of overlap integrals between the distinct set of LUOs, i.e., between $\{\phi_{ik}, \overline{\phi}_{ik}\}$ and $\{\phi_{jl}, \overline{\phi}_{jl}\}$ $(k, l = 1, 2, \ldots, g)$. Obviously, $S_{ij}^{\text{comm}} = 1$ as the common set of LUOs are mutually orthogonal to each other. Hence, the overlap between Ψ_i and Ψ_j is reduced to

$$S_{ij} = S_{ij}^{\text{diff}} = \big|\langle\phi_{ik}|\phi_{jl}\rangle\big|^2 \qquad (k, l = 1, 2, \ldots, g;\;\; g \leqslant m) \tag{S36}$$

The equation concludes that the computation of the overlap between two LSDs can be reduced to calculating the overlap between the distinct parts of the two LSDs. As a corollary, if the distinct parts of two Lewis structures have no atoms in common, then they are orthogonal to each other.

Now, let us look at the Hamiltonian integral between two LSDs, Ψ_i and Ψ_j, in a closed-shell system. Following the similar procedure used for the overlap integral of two Lewis structures, we can likewise arrive at

$$H_{ij} = 2\sqrt{S_{ij}}\Big(\sum_{r=1}^{h}\langle\phi_r|\hat{h}|\phi_r\rangle\,\big|\langle\phi_{ik}|\phi_{jl}\rangle\big| + \sum_{r=1}^{g}\big|\langle\phi_{ik}|\hat{h}_r|\phi_{jl}\rangle\big|\Big) \qquad (k, l = 1, 2, \ldots, g) \tag{S37}$$

As we can see, $\langle\phi_r|\hat{h}|\phi_r\rangle = \epsilon_r$ is the energy of LUO ϕ_r; $\big|\langle\phi_{ik}|\phi_{jl}\rangle\big| = \sqrt{S_{ij}^{\text{diff}}}$ is computed among the distinct LUOs only; $\left|\langle\phi_{ik}|\hat{h}_r|\phi_{jl}\rangle\right| = H_{ij}^{\mathrm{diff,r}}$ also corresponds the distinct LUOs only. Recalling that $S_{ij} = S_{ij}^{\mathrm{diff}}$ (eq S36), we can rewrite eq S37 as

$$H_{ij} = 2S_{ij}^{\mathrm{diff}}\sum_{r=1}^{h}\epsilon_r + 2\sqrt{S_{ij}^{\mathrm{diff}}}\sum_{r=1}^{g}H_{ij}^{\mathrm{diff,r}} \tag{S38}$$

As ϵ_r is the energy of LUO ϕ_r, $2\sum_{r=1}^{h}\epsilon_r = E_{ij}^{\mathrm{comm}}$ is the total energy of all the common LUOs shared by Ψ_i and Ψ_j. Meanwhile, according to eq S25, the last term in eq S38 equals H_{ij}^{diff}, the Hamiltonian integral calculated from the determinant associated with the distinct set of LUOs between Ψ_i and Ψ_j. As a result, eq S38 is simplified as

$$H_{ij} = S_{ij}^{\mathrm{diff}}E_{ij}^{\mathrm{comm}} + H_{ij}^{\mathrm{diff}} \tag{S39}$$

This equation suggests that the Hamiltonian integral between two Lewis structures is divided into two contributions: the total energy of the common part multiplied by the overlap of the distinct parts, and the Hamiltonian integral between the distinct parts. As a consequence, if two Lewis structures are orthogonal to each other, their Hamiltonian integral vanishes.

4 Löwdin weights for purely ionic HX molecules

As shown in the main text, the 2c-2e resonance system in the HX molecule is described by three Lewis structures: H—X ↔ H^+ :X^- ↔ H^-: X^+ (numbered as 1, 2, and 3, respectively). In the current WFRT framework, it is readily to obtain the overlap matrix of the LSDs as

$$\mathbf{S} = \begin{pmatrix} 1 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 1 & 0 \\ \frac{1}{2} & 0 & 1 \end{pmatrix} \tag{S40}$$

For a (hypothetic) purely ionic HX system, e.g., H^+ :X^-, the wave function expansion coefficients are (by substituting $q = 1$ in eqn (15) in the main text):

$$\mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \tag{S41}$$

which clearly indicates that the wave function of the purely ionic HX system is fully represented by the Lewis structure H^+ :X^-.

The Löwdin weights[8,9] are then obtained by means of symmetric orthogonalization of the LSDs. The new coefficients after symmetric orthogonalization are given as

$$\tilde{\mathbf{C}} = \mathbf{S}^{-\frac{1}{2}}\mathbf{C} = \begin{pmatrix} 0.2706 \\ 0.9619 \\ -0.0381 \end{pmatrix} \tag{S42}$$

As a result, the Löwdin weights for the three Lewis structures are the square of the coefficients: $w_1 = 0.0732, w_2 = 0.9253, w_3 = 0.0014$.

5 Distribution of weights of Lewis structures for naphthalene

Fig. S1 presents the weight of each individual Lewis structure (lower panel, blue line) and the accumulated weight (upper panel, red line) with the increasing number of Lewis structures, for naphthalene calculated at the B3LYP/Def2-TZVPP level. The Lewis structures along the x-axis are arranged by the number of lone pairs (λ) and in descending order of individual weight.

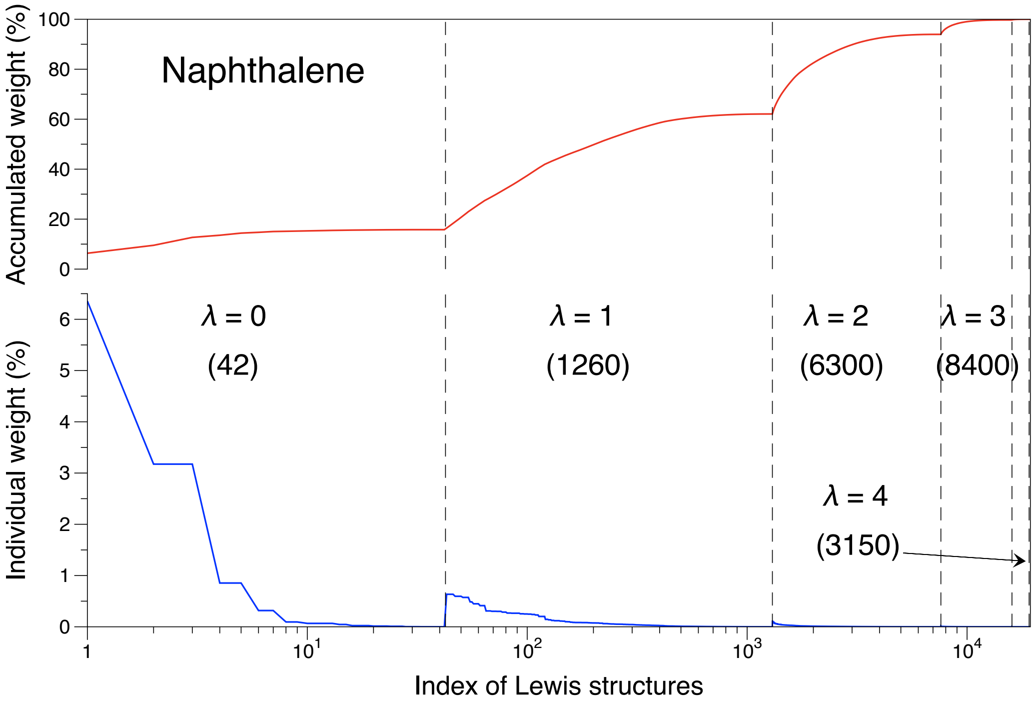

Figure S1. PWSO weight of each individual Lewis structure of naphthalene and the corresponding accumulated weight with the increasing number of Lewis structures. The Lewis structures are ordered along the x-axis by the number of lone pairs (λ), and within each same λ arranged in descending order of individual weight. The number in parentheses indicates the number of Lewis structures with the same number of lone pairs, λ.

Comparing the individual weights, we see that the Kekulé structures (the leftmost three points in Fig. S1) have a significantly higher weight than all other Lewis structures. Thus, the Kekulé structures can be regarded as the most dominant contributors. On the other hand, the accumulated weight presented in the upper panel of Fig. S1 (red curve) helps us understand why the few leading Lewis structures (the ones shown in Fig. 7 in the main text) only contribute a small percentage to the total weight. As we can see, there exist a great number of Lewis structures, each having a non-negligible (though small) weight, and they make a considerable contribution to the total weight. This accumulative effect is particularly obvious for the monoionic Lewis structures ($\lambda = 1$), as shown by the substantial increase of the accumulated weight (red curve) in the $\lambda = 1$ region. Note that the scale of x-axis is logarithmic, implying that the increase is over a large number of structures.

References

(1) Moffitt, W.; Scanlan, J.; Rideal, E. K. Some calculations on the ethylene molecule. *Proc. R. Soc. Lond. A* **1953**, *218*, 464–486.

(2) Karafiloglou, P.; Ohanessian, G. Understanding molecular orbital wave functions in terms of resonance structures. *J. Chem. Educ.* **1991**, *68*, 583.

(3) Karafiloglou, P. A method to calculate the weights of nbo electronic structures from Moffitt's theorem. *J. Comput. Chem.* **2001**, *22*, 306–315.

(4) Shaik, S.; Hiberty, P. C. *A Chemist's Guide to Valence Bond Theory*; John Wiley & Sons: Hoboken, New Jersey, 2007.

(5) Löwdin, P.-O. Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction. *Phys. Rev.* **1955**, *97*, 1474–1489.

(6) Leasure, S. C.; Balint-Kurti, G. G. Valence-bond theory and the evaluation of electronic energy matrix elements between nonorthogonal Slater determinants. *Phys. Rev. A* **1985**, *31*, 2107–2113.

(7) Chirgwin, B. H.; Coulson, C. A.; Randall, J. T. The electronic structure of conjugated systems. VI. *Proc. R. Soc. Lond. A* **1950**, *201*, 196–209.

(8) Löwdin, P. On the Non-Orthogonality Problem Connected with the Use of Atomic Wave Functions in the Theory of Molecules and Crystals. *J. Chem. Phys.* **1950**, *18*, 365–375.

(9) Löwdin, P.-O. On the Nonorthogonality Problem. *Adv. Quantum. Chem.* **1970**, *5*, 185–199.