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Remarkably Simple Relationship Connecting the Calculated Geometries of Isomolecular States of Three Different Multiplicities†

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We argue that for a large class of molecules, M, there exists an unexpectedly simple relationship among the calculated values of bond lengths in M_0 (its ground singlet state), M_T (its first excited triplet state), $M^{\bullet -}$ (the ground-state doublet of its radical anion), and $M^{\bullet +}$ (the ground-state doublet of the related radical cation). An estimate of the equilibrium bond length $\bar{R}$ for given bond in M_T may be obtained as follows: $\bar{R}(M_T) = \bar{R}(M^{\bullet -}) + \bar{R}(M^{\bullet +}) - \bar{R}(M_0)$. The accuracy of the $R(M_T)$ so calculated is usually 0.01−0.03 Å, less than 10% of whole range of distances for the species considered. The error is usually larger for small basis sets and for semiempirical parametrizations but is almost basis-set-independent for medium (D95, 3-21G) and large basis sets (6-31G, 6-31G*, 6-31G**, 6-311G**). The above equation may be qualitatively understood recognizing the "paired" properties of HOMO and LUMO in alternant hydrocarbons. We approach a quantitative rationalization of the relation from a general perspective of one-electron operators. Any property that can be represented by a one-electron operator should be subject to such a simple relationship. However, equilibrium bond lengths are not represented by one-electron operators. Instead, upon introduction of the empirical notion that equilibrium bond lengths are linear in bond order, the simple equation can be justified as an excellent approximate form. Several other relationships, still reasonably rooted in the shape of potential energy surfaces, do not fit as well. The simple relation applies exclusively to bonds constituting the chromophore part of a molecule and works best for systems with conjugated double bonds.

I. Introduction

Consider a typical molecule M containing $2N$ electrons. Let its ground singlet state be represented by a single ASMO (antisymmetrized molecular orbital) configuration in which each of the two spin orbitals of N MOs is occupied. Then take the two excited states built from the singly excited configuration made by promoting an electron from the HOMO to the LUMO, namely, $M(S_1)$ and M_T. Join with these the related radical cation containing $2N - 1$ electrons (the HOMO is half-occupied) and the radical anion with $2N + 1$ electrons (the LUMO is half-occupied). For any M we shall designate the five entities (states/species) $\{M_0, M_T, M_S, M^{\bullet -}, M^{\bullet +}\}$ an *isomolecular* family. The electronic structure of each member of a family is defined at a *common* specified set of nuclear coordinates using only these single ASMO configurations, as shown in Figure 1.

The chemical and physical properties of the species in Figure 1 differ markedly, of course. M_0 is usually a thermodynamically stable entity. $M^{\bullet -}$ and $M^{\bullet +}$ are commonly short-lived,[1] not because of thermodynamic reasons per se, but because of their high chemical reactivity, a consequence of their characteristic unpaired electron. The states and molecules of Figure 1 usually differ significantly in geometry. Also, the charge distribution in them varies, and this affects their chemical reactivity through thermodynamics. For example, as Förster's rule tells us,[2] excited states are both better electron donors and better electron acceptors than the corresponding ground state.

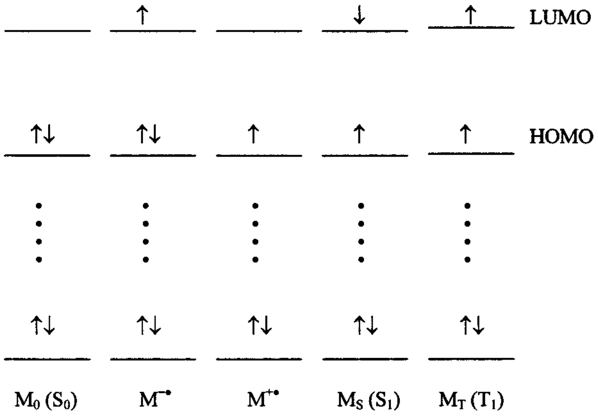

Figure 1. HOMO and LUMO orbital occupation diagram for M_0, $M^{\bullet -}$, $M^{\bullet +}$, M_T, and M_S in the case when M_0 is a closed-shell species.

In the literature these species, admittedly related, are often treated separately, since interest in them is often derived from very different areas of chemistry. We found only two papers where simultaneously optimized geometries for M_0, $M^{\bullet -}$, $M^{\bullet +}$, and M_T were reported.[3,4] Most studies focus on the comparative photochemical properties (considering M_0, M_T, M_S, and higher excited states),[5−7] while others concentrate on properties of the charged radicals[8,9] or on comparison of the radicals with the ground state of the neutral molecule.[10]

Might it be useful to examine a set of such five species together as a group or a family? We think so. There are experimental data suggesting that in some respects there is a close relationship between $M^{\bullet -}$ and $M^{\bullet +}$. In many cases it appears that the electronic spectra of $M^{\bullet -}$ and $M^{\bullet +}$ are strikingly similar.[11] This similarity is sometimes so pronounced that one

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† Dedicated to our friend, Bill Goddard.

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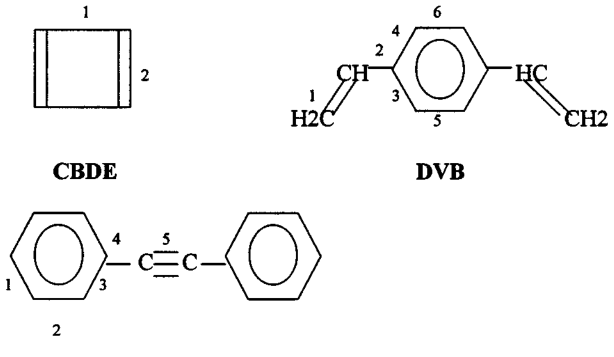

CBDE

DVB

DPA

Figure 2. Chemical formulas of 3 of the 14 isomolecular families investigated in this paper. The bond numbering used is indicated.

can almost overlap UV−vis spectra of $M^{\bullet -}$ and $M^{\bullet +}$, as in the case of naphthacene.[12]

Interestingly, the vibrational (IR) spectra of pentacene radical anions and radical cations isolated in solid matrices are also similar to each other,[13] suggesting a similar geometry and force field for both species. The same is true for the ESR spectra of many $M^{\bullet -}$ and $M^{\bullet +}$ species.[14] In fact, computations within the spirit of a classical Hückel method result in very similar optimized geometries of $M^{\bullet -}$ and $M^{\bullet +}$ for a large group of alternant hydrocarbons.[15] Interestingly, one may also find examples when the electronic spectra of $M^{\bullet -}$ and M_T are similar to each other.[16] The same is true for $M^{\bullet +}$ and the corresponding singlet dianions M^{2-}, not considered here in more detail.[11]

Properties of One-Electron Operators. What might cause such striking spectral and geometric similarities of $M^{\bullet -}$ and $M^{\bullet +}$ and, as we shall see, of M_0 and M_T?

Let us examine how any desired property *A*, provided it is expressible as a one-electron operator $\hat{A}$, is given for each member of the family. A universal relationship is sought for any such property across any isomolecular family M.

Any one-electron operator is represented by a sum over all electrons of individual operators each acting in the space of only one of the electrons present in the system. Such operators are ubiquitous. They represent all of the electric and magnetic dipole and multipole properties of a system, inductive effects due to substituents, and all vibronic effects to be encountered including force fields. The electronic energy of the system, because of the two-electron Coulomb terms in the Hamiltonian, is not a one-electron operator. The diagonal and off-diagonal matrix elements for any $\hat{A}$ in a basis of Slater spin orbital determinants for any ground-state and singly excited configurations may be written directly using the first-order density operator.[17]

For any property *A* one immediately finds

$$A(M_S) = A(M_T) = A(M_0) - A(\text{HOMO}) + A(\text{LUMO}) \tag{1}$$

$$A(M^{\bullet +}) = A(M_0) - A(\text{HOMO}) \tag{2}$$

and

$$A(M^{\bullet -}) = A(M_0) + A(\text{LUMO}) \tag{3}$$

in which *A*(HOMO) and *A*(LUMO) are the matrix elements of property $\hat{A}$ in the HOMO and LUMO orbitals, respectively. These orbital properties may be eliminated among the three equations to arrive at the sought for universal relationship for any (one-electron) property across any isomolecular group of species as defined above. Since any (one-electron) property must have the same value in the S_1 state as in the T_1 state (eq 1), we have $A(M_S) = A(M_T)$ and we may define this simply as A_{ST}. In a similarly simplified notation we write $A(M_0) \equiv A_0$, $A(M^{\bullet -}) \equiv A_-$, and $A(M^{\bullet +}) \equiv A_+$. The general relationship may be written in several entirely equivalent ways:

$$A_{ST} + A_0 - A_+ - A_- = 0 \tag{4a}$$

$$A_{ST} - A_+ = A_- - A_0 \tag{4b}$$

$$A_{ST} - A_- = A_+ - A_0 \tag{4c}$$

$$A_{ST} + A_0 = A_+ + A_- \tag{4d}$$

$$A_{ST} = A_+ + A_- - A_0 \tag{4e}$$

Each of these formulations has its distinct interpretative advantages. In eq 4a the properties across the family must algebraically sum to zero. In eqs 4b and 4c the "property gaps" between specific pairs of species must be identical. In eq 4d two specific pairwise summed properties must be identical. In eq 4e the property in one species (in this case the first excited singlet and triplet state) is determined by its values in the remaining three species).

Importantly, these relationships are valid only for a nuclear geometry that is *common* for all five members of the family. This is the geometry for which the electronic configurations shown in Figure 1 are defined. It need not be the equilibrium configuration of any one of them or it may be that of just one. This issue becomes important to our discussion later.

In the absence of the two-electron operator in the Hamiltonian (seen as Coulomb and exchange integrals in the energy) even the energy operator of the system becomes "one-electron " and eq 4a for energy is then valid to give

$$E(M_S) = E(M_T) = E(M^{\bullet +}) + E(M^{\bullet -}) - E(M_0) \tag{5}$$

This is clearly not an approximation of chemical and spectroscopic value. But for one-electron operators, expressions such as eqs 4 and 5 are very useful.

Distances. Inspired by eq 5,[18] one might take a big conceptual jump from energies to distances. Could it be that a relationship similar to eq 5 exists for the equilibrium bond lengths *R* in these species? Thus, might it be true that

$$\bar{R}(M_S,M_T) = \{\bar{R}(M^{\bullet -}) + \bar{R}(M^{\bullet +}) - \bar{R}(M_0)\} \tag{6}$$

This relationship makes qualitative sense in a simplistic one-electron picture for diatomic molecules. The positive ion, which has a hole in the HOMO (usually a bonding orbital), and the negative ion, which has an electron in the LUMO (usually an antibonding orbital typically paired with the HOMO), should indeed have similar properties. Since the LUMO is more antibonding than the HOMO is bonding (once overlap is included), the given bond elongation in $M^{\bullet -}$ (compared to that in M_0) should be slightly larger than for $M^{\bullet +}$. The elongation should be magnified in the two singly excited states, M_0 and M_T, both of which have a hole in the HOMO and an electron in the LUMO. Toward the end of the paper this argument is explored more formally, particularly with regard to a bond-order−bond-length relationship.

TABLE 1: Computed Values of C−C Bond Lengths ($\bar{R}_{C-C}$/Å) for M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Forms of C_2H_4 (6-31G Basis Set Was Used)**

computed $\bar{R}_{C-C}$/Å				$\bar{R}_T$			
M_0	$M^{\bullet-}$	$M^{\bullet+}$	M_T	calc (eq 6)/Å	abs error/Å	range/Å	rel error/%
1.316	1.435	1.402	1.534	1.521	−0.013	0.218	−6.0

A computational investigation of the validity of the simple algebraic linear relationship of eq 6 for a large and diverse number of isomolecular families is the main aim of this paper.

II. Methods of Calculations

We have performed calculations for the following families: C_2, acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), N_2H_2, B_2H_2, CO, CN^-, N_2, NO^+, butadiene, cyclobutadiene (CBDE), and 1,4-*cis*-divinylbenzene (DVB). Published data for diphenylacetylene (DPA)[3] were also examined, giving a total of 14 families examined. The chemical formulas of CBDE, DVB, and DPA together with a bond numbering convention used herein are presented in Figure 2.

We have optimized molecular geometries for the M_T, $M^{\bullet-}$, $M^{\bullet+}$, and M_0 at the UHF SCF level of theory. A 6-31G** basis set for C_2, C_2H_2, C_2H_4, C_2H_6, N_2H_2, B_2H_2, CO, CN^-, N_2, NO^+, and CBDE was employed. In addition, we used a broad range of basis sets for N_2H_2 in order to determine the effect of the basis set on the final result.

For CBDE and DVB we used the AM1 semiempirical parametrization.[19] In the literature are found data for DPA with a 4-31G basis set and the ROHF SCF method.[3]

Equation 6 gives us in principle the freedom to choose which of the excited states (M_S or M_T) is to be compared to the "hybrid" of $M^{\bullet-}$, $M^{\bullet+}$, and M_0. For simplicity we have decided to choose the M_T and not the M_S state. Most of the simpler quantum chemical programs available can easily optimize the geometry of both M_T and M_0 but not of M_S. Calculations for M_S (and higher excited singlet states S_n) require orthogonalization to the M_0 state[20] and usually consume much computational time.

All calculations were performed with the HyperChem 5.0 package.

III. Results: Computations and Test of Eq 6

To test eq 6, we have optimized the geometries of M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ species for 14 isomolecular families.

III.1. Geometries of M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Forms of C_2H_4. For an initial test of the validity of eq 6, we have chosen a simple organic molecule: ethylene (C_2H_4). Table 1 shows the calculated C−C bond lengths for the M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ forms of C_2H_4. We show also the value of $\bar{R}_T$ computed according to eq 6 ("calc" in Table 1) as well as the discrepancy between this and the $\bar{R}_T$ obtained for M_T in ab initio optimization ("error" in Table 1 and in the rest of the tables). To display the error in the predicted bond length within the context of the available spread of bond lengths found within a given family, we report the percentage error. This "relative error" (%) is defined as "error" divided by the total range of the C−C bond length among four species considered (the difference between the longest and the shortest C−C bond in the entire series). The same definitions are used in all tables hereafter.[21]

The data in Table 1 show that the $\bar{R}_{C-C}$ obtained for M_T according to eq 6 is in good agreement with that computed ab initio (the error reaches ca. 0.01 Å, which is only 6% of total bond length range).

TABLE 2: Computed C−C Bond Lengths ($\bar{R}_{C-C}$/Å) for M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Forms of CBDE (6-31G Basis Set Was Applied)**

	computed $\bar{R}_{C-C}$/Å				$\bar{R}_T$			
bond no.	M_0	$M^{\bullet-}$	$M^{\bullet+}$	M_T	calc (eq 6)/Å	abs error/Å	range/Å	rel error/%
1	1.318	1.378	1.363	1.426	1.423	0.003	0.108	2.6
2	1.565	1.501	1.489	1.426	1.425	0.001	0.139	0.7

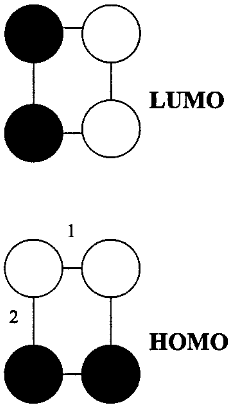

Figure 3. Shape of HOMO and LUMO orbitals of CBDE together with the bond numbering scheme (the relative bond lengths are exaggerated in the drawing).

Two further observations may be made from the calculations for C_2H_4. First, as postulated in the Introduction, $\bar{R}(M_T) > \bar{R}(M^{\bullet-}) > \bar{R}(M^{\bullet+}) > \bar{R}(M_0)$, namely, 1.534 > 1.435 > 1.402 > 1.316. As we will show below, a similar ordering rule for bond lengths will be qualitatively fulfilled in most of the cases investigated. Second, eq 6 is best applied[22] to bonds associated with the chromophoric part of a molecule. Thus, the relationship is not reliable for C−H bonds, even in cases where the CC bonds are well predicted (data not shown).

III.2. Geometries of M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Forms of CBDE and DVB. Ethylene is the simplest molecular system containing a C═C double bond. Next we studied cyclobutadiene (CBDE) with its two conjugated double bonds. Table 2 presents computational data for CBDE.

As one can see from Table 2, the C−C bond lengths calculated according to eq 6 agree quite well with the C−C bond lengths computed for the M_T state with a Hartree−Fock SCF procedure. The error is ≤0.003 Å, this being only 2.6% of the total variability of C−C bond lengths in the four species examined. Moreover, the qualitative relationship observed above for ethylene, $\bar{R}(M_T) > \bar{R}(M^{\bullet-}) > \bar{R}(M^{\bullet+}) > \bar{R}(M_0)$, is now fulfilled for bond 1 of CBDE. The "opposite" relation, i.e., $\bar{R}(M_T) < \bar{R}(M^{\bullet-}) < \bar{R}(M^{\bullet+}) < \bar{R}(M_0)$, is found for bond 2 of CBDE. These two relations are the consequence of the shape of the HOMO and LUMO of CBDE (Figure 3). Frontier orbitals ideas serve effectively in this case.

Another system with two conjugated double bonds—butadiene—is much changed in geometry in its triplet state; it is no longer planar. Results based on eq 6 now are substantially in error, similar to the acetylene case (see section III.5).

To explore the applicability of eq 6 to bigger systems, we carried out semiempirical (AM1) calculations for larger molecules, such as divinylbenzene (DVB, Figure 1). We also used the existing data set for diphenylacetylene (DPA, Figure 1), obtained with a small 4-31G basis set. We also performed AM1 calculations for CBDE, previously optimized with a HF method. Table 3 shows computational data for these three molecules.

As may be seen from Table 3 (results for DVB), eq 6 is also satisfied quite well when semiempirical calculations are used.

TABLE 3: Computed C−C Bond Lengths ($\bar{R}_{C-C}$/Å) for the M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Members of the CBDE, DVB, and DPA Isomolecular Families[a]

	computed $\bar{R}_{C-C}$/Å				$\bar{R}_T$			
	M_0	$M^{\bullet-}$	$M^{\bullet+}$	M_T	calc (eq 6)/Å	abs error/Å	range/Å	rel error/%
				CBDE				
1	1.449	1.440	1.450	1.440	1.440	0.000	0.010	1.2
2	1.449	1.440	1.450	1.440	1.440	0.000	0.010	1.2
				DVB				
1	1.335	1.358	1.354	1.377	1.377	0.000	0.042	0.7
2	1.458	1.427	1.427	1.398	1.396	0.002	0.06	3
3	1.405	1.430	1.429	1.456	1.454	0.003	0.05	6
4	1.404	1.429	1.429	1.456	1.454	0.003	0.05	6
5	1.390	1.373	1.368	1.349	1.352	0.002	0.04	5
6	1.392	1.374	1.370	1.350	1.352	0.002	0.04	5
				DPA				
1	1.384	1.394	1.394	1.402	1.404	+0.002	0.020	+10
2	1.381	1.372	1.370	1.359	1.361	+0.002	0.022	+9.0
3	1.392	1.424	1.413	1.443	1.445	+0.002	0.051	+3.9
4	1.431	1.387	1.384	1.341	1.340	−0.001	0.090	−1.1
5	1.194	1.224	1.224	1.257	1.254	−0.003	0.063	−4.8

[a] Bond numbering according to Figure 1.

TABLE 4: Equilibrium N−N Bond Lengths (R_{N-N}/Å) for M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Members of the *trans*-N_2H_2 Isomolecular Family[a]

	computed R_{N-N}/Å				R_T			
method/ basis set	M_0	$M^{\bullet-}$	$M^{\bullet+}$	M_T	calc (eq 6)/Å	abs error/Å	range/Å	rel error/%
3-21G	1.3058	1.410	1.148	1.286	1.256	−0.032	0.262	−12.3
6-31G*	1.216	1.354	1.141	1.254	1.279	+0.025	0.213	11.7
6-31G**	1.216	1.354	1.141	1.253	1.279	+0.026	0.213	12.2
6-311G**	1.212	1.354	1.136	1.251	1.278	+0.027	0.217	12.4
D95V	1.221	1.360	1.145	1.259	1.284	+0.024	0.215	11.4
CNDO	1.224	1.283	1.183	1.258	1.243	−0.016	0.100	−15.8
INDO	1.230	1.292	1.186	1.241	1.249	0.008	0.106	7.2
AM1	1.212	1.279	1.154	1.214	1.221	0.007	0.125	5.6
PM3	1.219	1.308	1.165	1.245	1.254	0.010	0.144	6.7

[a] Results obtained with UHF SCF for ab initio calculations with a variety of basis sets and for semiempirical calculations (CNDO, INDO, AM1, PM3) using different parametrizations.

The biggest error in evaluation of the C−C bond length for DVB (M_T) was 0.0034 Å, this being 6% of the total variability of C−C bond lengths. Note also an interesting phenomenon: the semiempirical method produced an evidently incorrect square (and not rectangular) structure for CBDE in its M_0 state. Even in this case eq 6 worked properly. It is noteworthy that eq 6 produces reliable results also for DPA, although this system contains a triple bond, albeit one built into a more extended delocalized π system (compare results for acetylene from section III.5).

III.3. Geometries of M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Forms of N_2H_2. To examine whether eq 6 also may apply to π systems containing main group atoms other than C, the nitrogen analogue of ethylene, i.e., N_2H_2, has been studied. Calculations were done with a variety of ab initio basis sets and semiempirical parametrizations. A summary of the results is found in Table 4.

With the complete neglect of differential overlap (CNDO) method and also for the smallest basis set used (3-21G), the errors are significant and negative. The remaining calculations report errors of similar magnitude but positive. In most cases the eq 6 value for $\bar{R}_{N-N}$ of M_T remains within 0.03 Å of that obtained in quantum mechanical computations. Interestingly, despite change in a typical order, $\bar{R}(M_T) > \bar{R}(M^{\bullet-}) > \bar{R}(M^{\bullet+}) > \bar{R}(M_0)$, reasonable results were nevertheless obtained. Moreover, the small values of percentage error point out the utility of eq 6, regardless of the basis set used. It appears that eq 6 also may be applied to heteroatomic π systems.

TABLE 5: a−b Bond Lengths (R_{ab}/Å) for M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Members of C_2^{2-}, CO, CN^-, N_2, NO^+, and O_2^{2+} Isomolecular Families[a]

	computed R_{ab}/Å				R_T			
family	M_0	$M^{\bullet-}$	$M^{\bullet+}$	M_T	calc (eq 6)/Å	abs error/Å	range/ Å	rel error/%
CC^{2-}	1.266	1.278	1.253	1.270	1.265	−0.005	0.026	−20.0
CO	1.114	1.217	1.098	1.196	1.201	+0.004	0.119	+3.6
CN^-	1.161	1.270	1.162	1.268	1.272	+0.004	0.110	+3.3
N_2	1.078	1.172	1.094	1.187	1.193	+0.006	0.115	+5.1
NO^+	1.040	1.127	1.133	1.194	1.220	+0.025	0.154	+16.4
OO^{2+}	0.990	1.062	1.117	1.123	1.188	−0.065	0.133	−50

[a] Here, the simple state notation needs clarification. The net charge on each member of a given family must be raised or lowered according to the charge on the reference state, M_0. Accordingly, net charge on M_0 is −2 for C_2^{2-}, −1 for CN^-, +1 for NO^+, and +2 for O_2^{2+}.

TABLE 6: Computed Values of C−C Bond Lengths ($\bar{R}_{C-C}$/Å) for M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Members of the C_2 and C_2H_2 Isomolecular Families (6-31G Basis Set Was Used)**

	computed $\bar{R}_{C-C}$/Å				$\bar{R}_T$			
	M_0	$M^{\bullet-}$	$M^{\bullet+}$	M_T	calc (eq 6)/Å	abs error/Å	range/Å	rel error/%
C_2	1.303	1.281	1.288	1.292	1.266	−0.026	0.02	−100
C_2H_2	1.186	1.299[a]	1.230	1.322	1.342	+0.021	0.14	+14.8
C_2H_2	1.186	1.271[b]	1.230	1.322	1.315	−0.007	0.14	−5

[a] Corresponding to the bent structure at the energy minimum. [b] Corresponding to a linear structure, a saddle point between two equivalent bent minima.

III.4. Geometries of M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Forms of Isoelectronic CO, CN^-, N_2, NO^+ Isomolecular Families. We next performed ab initio calculations for the isoelectronic families C_2^{2-}, CO, CN^-, N_2, NO^+, and O_2^{2+}. Table 5 summarizes the results obtained.

The accuracy of eq 6 is evident for CO, CN^-, and N_2. Errors reach typically 0.005 Å, corresponding to a relative error of 5% or less. Substantially higher relative errors are observed for NO^+, C_2^{2-}, and O_2^{2+} (16−50%). It may be that electrostatic effects in the highly charged C_2^{3-} and O_2^{3+} radical species are not properly accounted for.

III.5. Geometries of M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ Forms of Isomolecular Families C_2, C_2H_2, and C_2H_6. In an effort to better understand why the simple linear relationship (eq 6) brings us so easily to the geometry of M_T for so many families, we searched for exceptions from this rule. These already were apparent among very simple isomolecular families based on C_2, C_2H_2, and C_2H_6. Table 6 shows the calculated C−C bond lengths for the M_0, M_T, $M^{\bullet-}$, and $M^{\bullet+}$ members of the C_2 and C_2H_2 families.

Neither for C_2H_2 nor for C_2 do we obtain the desired agreement. For C_2H_6 (data not presented in Table 1) attempts to obtain a M_T geometry led to fragmentation to the ethyl radical and $H^{\bullet}$. For acetylene the equilibrium geometry of $M^{\bullet-}$ is not linear but is a bent, trans-type structure. We do obtain 5% agreement between calculated (eq 6) and computed values of $\bar{R}_{C-C}$ for C_2H_2 but for a geometry of the radical anion that is not stable, namely, that of the linear transition state between two bent minima.

While eq 6 succeeds for C_2H_4 (section III.1), it basically fails for this set of isomolecular families. These are circumstances where it fails. (i) One circumstance is when the *calculated* ground state is not a singlet state, as assumed in our preliminary

TABLE 7: Testing Eqs 10 and 11 for Isomolecular Families CN^-, N_2, and CO (UHF, 6-31G Basis Set)**

	M_0		$M^{\bullet +}$		$M^{\bullet -}$		M_T		$\bar{R}_T$/Å				k_T/mdyn Å^{-1}	
family	$\bar{R}$/Å	k/ mdyn Å^{-1}	$\bar{R}$/Å	k/ mdyn Å^{-1}	$\bar{R}$/Å	k/ mdyn Å^{-1}	$\bar{R}$/Å	k/ mdyn Å^{-1}	eq 6	error, eq 6	eq 11	error, eq 11	eq 10	error, eq 10
CN^-	1.161	42.18	1.1620	23.55	1.270	29.68	1.268	17.60	1.272	0.004	0.915	−0.353	11.05	−6.55
N_2	1.0781	62.91	1.094	54.26	1.172	38.70	1.193	32.49	1.187	−0.006	1.135	−0.058	30.05	−2.44
CO	1.114	47.10	1.098	45.33	1.217	26.94	1.196	23.60	1.201	0.004	1.275	0.078	25.17	+1.57

considerations. This happens for C_2 (and also for B_2H_2; results not shown here), where the ground state is calculated (erroneously[23]) to be a triplet state,[24] as well as in two cases when the geometry of one of the family members strongly differs in structure from that of the others, as exemplified by (ii) C_2H_2 (the molecule bends when an electron is added to it) and (iii) C_2H_6 (this system is unstable to fragmentation in the triplet state, according to calculations).

It may be that the optimal preconditions for the application of eq 6 to organic systems are likely to be found in systems with double bonds. Families having cumulated double bonds might have to be excluded as well, as we have found for computations (not shown) on the allene and CO_2 families, where eq 6 fails badly.

Next, we briefly search for an explanation of why eq 6 succeeds as well as it does for such an impressive array of isomolecular families.

IV. Can the Success of Eq 6 Be Rationalized?

IV.1. Why the Distance Formula, Eq 6, Should *Not* Work. As we have seen in section III, eq 6 proves to be a remarkably successful expression for linking equilibrium bond lengths among the four members of a diverse set of what we have called isomolecular families. Though in this presentation we have focused on predicting the equilibrium bond lengths of the lowest triplet state M_T in each family, the targeted species could have been any of the other members with the same outcome. In fact, an alternative approach in the presentation would have been to check the zero of eq 6 (i.e., where $\bar{R}(M^{\bullet -}) + \bar{R}(M^{\bullet +}) - \bar{R}(M_0) - \bar{R}(M_T) = 0$). The relative error for achieving the zero is identical to that given in the tables.

Is it possible that the equilibrium bond length is somehow representable by a one-electron operator? If so, then eq 6 would follow directly from the general eqs 4a−4e (see Introduction). According to one line of reasoning, the equilibrium bond length changes across a family does *not* appear to be, ironically, represented by a one-electron operator.

Let the equilibrium geometry of the members of any isomolecular family be specified in the language of the complete space of normal coordinates, $\bar{Q}_0$ for M_0, $\bar{Q}_{ST}$ for M_{ST}, $\bar{Q}_+$ for $M^{\bullet +}$, and $\bar{Q}_-$ for $M^{\bullet -}$. One can show for a harmonic oscillator[25] that for any state j ($j \equiv M_0, M_T, M_S, M^{\bullet -}, M^{\bullet +}$),

$$\bar{Q}_j = \bar{Q}_0 + \frac{\left(\frac{\partial V^j}{\partial Q}\right)_0}{k_j} \tag{7}$$

Here, the derivative of the nuclear potential energy for state j at $\bar{Q}_0$ is evaluated at the equilibrium nuclear structure of M_0 (any other reference structure common to all members of the family might have been used). It is just the component of force along Q (any one of $3N - {}^6/_5$) at $\bar{Q}_0$ on the jth potential energy surface. And k_j is the force constant along a given normal mode in state j. The latter is just

$$k_j = \left(\frac{\partial^2 V^j}{\partial Q^2}\right)_0 \tag{8}$$

also a property of state j at the equilibrium position, $\bar{Q}_0$, of M_0, though in the harmonic approximation the force constant does not depend on nuclear coordinates.

Now both the numerator (the force) and the denominator (the force constant) in the second term on the right-hand side (RHS) of eq 7, both being vibronic properties, *are* represented by one-electron operators.[17,26] Each should obey eqs 4a−4e to give (with obvious simplified notation) for the forces

$$\left(\frac{\partial V^{ST}}{\partial Q}\right)_0 = \left(\frac{\partial V^{+}}{\partial Q}\right)_0 + \left(\frac{\partial V^{-}}{\partial Q}\right)_0 \tag{9}$$

(the force in M_0 vanishes at Q_0) and for the force constants

$$k_{ST} = k_+ + k_- - k_0 \tag{10}$$

These two applications of eqs 4a−4e together with eq 7 lead to a universal expression relating the amplitudes of the equilibrium geometries (in normal coordinates) of the five members of any isomolecular family (provided the simple HOMO/LUMO electronic structure is valid). We obtain

$$\bar{Q}_{ST} = \frac{k_+}{k_{ST}}\bar{Q}_+ + \frac{k_-}{k_{ST}}\bar{Q}_- - \frac{k_0}{k_{ST}}\bar{Q}_0 \tag{11}$$

Since the equilibrium structure in terms of the normal coordinates relates linearly to the equilibrium structure expressed in terms of valence coordinates, such as the equilibrium bond lengths, an equation like eq 11 for the $\bar{R}_j$'s should follow.[27] The force constant scaling factors definitely vary with j, as found in our calculations. This spoils any chance of recovering eq 6.

We also note that a relationship identical to eq 11 has been recently derived by Ayers and Parr.[28]

To test eq 11, we calculate its prediction of $\bar{R}_T$ for three diatomic families CN^-, N_2, and CO. Also included is a test of eq 10 for the force constant as a one-electron property. In these diatomics the link between the one normal mode and the bond length is unambiguous, having a mass weighting that must be the same across the members of a given family.

As seen in Table 7, of the two routes to R_T, eq 6 is overwhelmingly favored over the “correct” eq 11. Furthermore, eq 10 for the force constants is only modestly acceptable, if at all. Thus, it is an empirical equation such as

$$\bar{Q}_{ST} \approx \bar{Q}_+ + \bar{Q}_- - \bar{Q}_0 \tag{12}$$

(equivalent to eq 6 and not eq 11) that holds such promise.

Failure of the simple ASMO state description (no CI) for the electronic states across any given family can be expected. That alone would invalidate eqs 10 and 11. But why the simpler substitute, eq 6 (or eq 12), might compensate for this to such a remarkable degree is not apparent.

IV.2. Why the Distance Formula, Eq 6, Might Work, In Fact. As hinted at in the case of ethylene (section III.1) and cyclobutadiene (section III.2), thinking in the spirit of MO theory points to a qualitative understanding of the relationship of eq 6. Even as we feel that a one-electron picture and the orbital-bonding power paradigm make the relationship credible, the reasons behind the quantitative success of the simple distance relationship are simply not obvious. The force constants for the four species under discussion are not even approximately equal. Among other things, the bond orders change so much. From our calculations we know that Koopmans' theorem, which inspired these findings, is not adequate for understanding the electronic energies of the members of each family. Why then should eq 6 work so well? Is it possible to rationalize the success of eq 6 (or its analogue) by another approach?

To begin with, recall that eqs 4a−4e refer to one-electron properties within the HOMO/LUMO configurational basis for describing the electronic structures (at a common nuclear configuration) for all members of any isomolecular family. Should more elaborate electronic descriptions be necessary, then eqs 4a−4e need not apply and simple relationships like eq 6 would appear to be all the more surprising. However, we have just seen how the equilibrium bond distances are not represented by one-electron operators. Therein lies the difficulty of rationalizing eq 6.

By contrast, bond order is a prototypical one-electron property. Empirical relationships between bond order and bond length are known. Might this be a route for rationalizing eq 6? We briefly examine this question.

Bond order (BO) is a prototypical one-electron property (see Appendix A). It may be defined in a variety of ways from classical π-electron bond orders through Pauling schemes to a Mulliken population analysis.[29] One way to set BO is just as a three-dimensional δ function in space for each electron summed over all electrons (see Appendix A). And in the LCAO-ASMO description the BO can be identified with individual bonds in a molecule. Thus, across any isomolecular family, one can immediately apply eqs 4a−4e and write, for example,

$$\mathrm{BO}_{\mathrm{ST}} = \mathrm{BO}_{+} + \mathrm{BO}_{-} - \mathrm{BO}_{0} \tag{13}$$

Now the literature has established empirical relationships between the bond order of a given bond and its bond length. And a particularly successful relationship is a linear one.[30] Might it be possible to transform eq 13 into an analogous expression for equilibrium bond length after all? It is crucial to recall that eqs 4a−4e refer to properties of members of an isomolecular family *at a common geometry*. Equation 13 thus holds for any nuclear configuration, but it is the same for all members of the family. We use eq 13 and convert each BO_j to one at the equilibrium bond length, different for each family member j.

In a relatively narrow region around the equilibrium bond length, a reasonable assumption is the linear relationship for each j:

$$R_j = R^0{}_j - z_j\,\mathrm{BO}_j \tag{14}$$

where z_j is the slope and $R^0{}_j$ is the intercept for member j. For the BO at any common bond length $R_j = R$, we have

$$\mathrm{BO}_j = (R^0{}_j - R)/z_j \tag{15}$$

and it is these BO_j's that should obey eq 13. At the same time we are interested in the properties at equilibrium positions $\bar{R}_j$, not at R. Thus, at $\bar{R}_j$ eq 14 becomes

$$\bar{R}_j = R^0{}_j - z_j\,\overline{\mathrm{BO}}_j \tag{16}$$

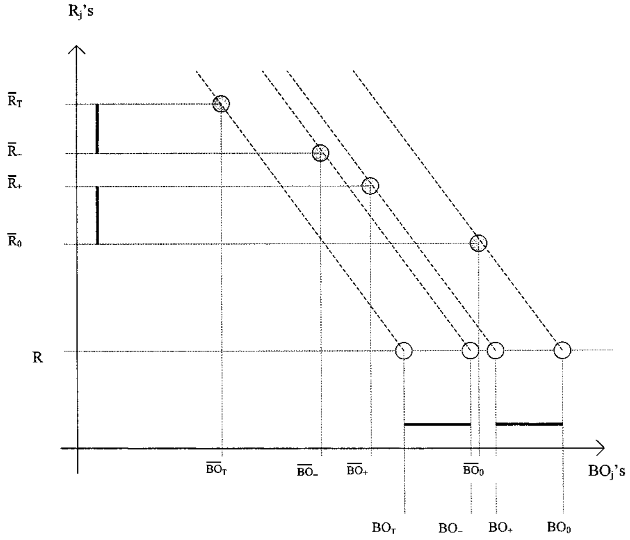

Figure 4. Illustration of eq 17 [and eq A8 (Appendix A)] with $z_j = z$.

and with eqs 15 and 16 we obtain

$$\mathrm{BO}_j = \overline{\mathrm{BO}}_j + (\bar{R}_j - R)/z_j \tag{17}$$

The above relationship describing R_j vs BO_j dependence during "relaxation" of species j from a given (and common) R to their equilibrium $\bar{R}_j$'s is illustrated in Figure 4.

Equation 13 now gives

$$\overline{\mathrm{BO}}_{\mathrm{ST}} + (R_{\mathrm{ST}} - R)/z_{\mathrm{ST}} = \overline{\mathrm{BO}}_{+} + (R_{+} - R)/z_{+} + \overline{\mathrm{BO}}_{-} + (R_{-} - R)/z_{-} - \overline{\mathrm{BO}}_{0} + (R_{0} - R)/z_{0} \tag{18}$$

which hardly appears to be useful. However, if we reasonably ask (see Figure 4) that the same bonds share the same slope with all members of the family, then with $z_j = z$, eq 18 is greatly simplified to

$$\bar{R}_{\mathrm{ST}} + \bar{R}_0 - \bar{R}_+ - \bar{R}_- = z(\overline{\mathrm{BO}}_{\mathrm{ST}} + \overline{\mathrm{BO}}_0 - \overline{\mathrm{BO}}_+ - \overline{\mathrm{BO}}_-) \tag{19}$$

Now since the present work has demonstrated that the left-hand side (LHS) of eq 19 vanishes with fairly high accuracy, then so must the right-hand side (RHS). Thus, empirically at least, eq 13 for the BO's at R holds also for the $\overline{\mathrm{BO}}_j$'s at the individual $\bar{R}_j$'s. We have not calculated the $\overline{\mathrm{BO}}_j$'s. Were these such as to cause the RHS of eq 19 to (even nearly) vanish, then this could be a novel route for supporting the linear R_j/BO_j relationship (eq 14).

Perhaps eq 19 also offers a more direct basis for making an argument because now the RHS of this equation might vanish. Thus, let us rewrite the RHS of eq 19 to focus on the competition between two BO "gaps":

$$(\overline{\mathrm{BO}}_{\mathrm{ST}} + \overline{\mathrm{BO}}_0 - \overline{\mathrm{BO}}_+ - \overline{\mathrm{BO}}_-) = (\overline{\mathrm{BO}}_0 - \overline{\mathrm{BO}}_+) - (\overline{\mathrm{BO}}_- - \overline{\mathrm{BO}}_{\mathrm{ST}}) \tag{20}$$

$(\overline{\mathrm{BO}}_0 - \overline{\mathrm{BO}}_+)$ is the BO gap between a filled HOMO (at $\bar{R}_0$) and the half-filled HOMO (at $\bar{R}_+$). The LUMO is vacant. $(\overline{\mathrm{BO}}_- - \overline{\mathrm{BO}}_{\mathrm{ST}})$ is also the BO gap between the filled HOMO (now at $\bar{R}_-$) and the half-filled HOMO (at $\bar{R}_{\mathrm{ST}}$). Only now the LUMO is occupied by one electron. To the extent that the effect on the BO of the added HOMO electron is in each case (practically) the same, we have reason to say that the RHS might vanish (or nearly so), thus supporting eq 6. However, if the LUMO is antibonding and the HOMO bonding, then the ($\overline{BO}_{-} - \overline{BO}_{ST}$) gap refers to bond lengths that are generally longer (weaker) than for the ($\overline{BO}_{0} - \overline{BO}_{+}$) gap. This suggests that ($\overline{BO}_{0} - \overline{BO}_{+}$) > ($\overline{BO}_{-} - \overline{BO}_{ST}$), but the inequality may be slight. Thus, the LHS of eq 19, whole small, should be on the positive side of zero. In fact, we have found that the relative error of the zero of eq 6 (measured for $\bar{R}_j$'s, not BO_j's), small as it is, is a positive one for 24 of the 31 bond lengths found in Tables 1−5.

In addition to the interesting regularities studied here, it is possible to derive relationships ordering any one-electron property across an isomolecular family. This is carried out in Appendix B.

V. Conclusions

We have carried out electronic structure calculations for a number of organic (C_2, C_2H_2, C_2H_4, C_2H_6, allene, cyclobutadiene, 1,4-*cis*-divinylbenzene**)** and main group heteroatom isomolecular families (N_2H_2, B_2H_2, C_2^{2-}, O_2^{2+}, CO, CN^-, N_2, NO^+, CO_2). For each we have optimized the geometries of its M_0 (S_0), $M^{\bullet -}$, $M^{\bullet +}$, and M_T (T_1) members at the UHF SCF level of theory, using mainly a 6-31G** basis set and the AM1 semiempirical parametrization (the latter for larger molecules).

Our data document that there exists a remarkably simple relationship between the computed equilibrium bond lengths for the members of each family, namely, $\bar{R}(M_T) = \bar{R}(M^{\bullet -}) + \bar{R}(M^{\bullet +}) - \bar{R}(M_0)$. This states that one may calculate the equilibrium bond length for M_T by adding the equilibrium bond lengths for the radical ions $M^{\bullet -}$ and $M^{\bullet +}$ and subtracting the equilibrium bond length for M_0. The absolute error of such a simple, indeed simplistic, calculation is usually much less than 0.03 Å (typically 5−10% of total range of bond lengths found across the members of one family).

The practical independence of this relationship on the dimension of the basis set was demonstrated for N_2H_2. Semiempirical quantum chemical methods may also be used, though they usually produce bigger errors.

We have established the remarkable simple distance relationship at a certain intermediate level of computational quantum chemistry. It remains to be determined whether the highest level of theory—or preferably experiment, though the data are often lacking—will confirm this regularity. Ayers and Parr, in work to be published,[28] have recently provided a density functional perspective on the conditions when the simple rule (eq 6) will hold.

The relationship discussed has severe and yet comprehensible limitations: it applies exclusively in cases when no qualitative changes of molecular geometry (other than distances) occur upon going from M_0 to M_T or upon ionization or electron attachment. Molecular systems free of such limitations are those with double and conjugated double bonds. For these the distance formula (eq 6) appears to apply best. A second limitation is that eq 6 is best applied to the chromophoric backbone of a molecule and not to the bonds only slightly affected by electronic excitation, ionization, or electron attachment (such as C−H bonds, for example), if only because it cannot accurately deal with minor changes in bond length.

Practical application of this simple relationship might be to construct, or anticipate, a good approximate geometry for triplet states prior to their exact optimization, thus effectively reducing computational time. Of course, there is nothing special about M_T as the "target" state. One could just as easily focus on any one of the four members (M_0, M_T, $M^{\bullet -}$, and $M^{\bullet +}$), provided the geometries of the remaining three forms are known. One might also look for detailed differences between the geometries of M_S and M_T states (representatives of the "excited state" in eq 6). Finally, the simple relationship may possibly be generalized to excited states not based simply on the HOMO and LUMO orbital pair but include states built of more excited configurations that involve other filled and unfilled MOs.

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Appendix A

Details of BO as a True One-Electron Property and the Validity of Eq 13 for Every Bond. The electron density operator is a true one-electron operator. It is given by

$$\rho_1 = \sum_{j=1}^{\text{all electrons}} \delta(\vec{r} - \vec{r}_j) \tag{A1}$$

and the universal equation for its expectation values (electron numbers) in each state must be of the form of eq 4, namely,

$$\rho_{ST} = \rho_{+} + \rho_{-} - \rho_{0} \tag{A2}$$

which says, trivially, that $2N = (2N - 1) + (2N + 1) - 2N$.

In fact, the matrix of the one-electron density operator in the AO basis of the LCAO-MO's is known as the charge/bond order matrix. To expose these AO details, it is best to return to eqs 1−3 for the electron density operator to write

$$\rho_{ST} = \rho_0 - \rho_{HOMO} + \rho_{LUMO} \tag{A3a}$$

$$\rho_{+} = \rho_0 - \rho_{HOMO} \tag{A3b}$$

$$\rho_{+} = \rho_0 + \rho_{LUMO} \tag{A3c}$$

in which ρ_{HOMO} and ρ_{LUMO} are just the "partial" MO charge/bond order matrix elements. We expose these in detail by writing

$$|HOMO\rangle = \frac{1}{{N_H}^{1/2}} \sum_{k=1}^{AOs} h_k |k\rangle \tag{A4a}$$

$$|LUMO\rangle = \frac{1}{{N_L}^{1/2}} \sum_{k=1}^{AOs} l_k |k\rangle \tag{A4b}$$

in which the normalization factors based on pure-real normalized basis AOs $\{|k\rangle\}$ with nonzero overlap are

$$N_H = \{\sum_{k=1} |h_k|^2 + \sum_{k \neq k'} S_{kk'}(h_k h_{k'}^{*} + h_k^{*} h_{k'})\} \tag{A5a}$$

and similarly,

$$N_L = \{\sum_{k=1} |l_k|^2 + \sum_{k \neq k'} S_{kk'}(l_k l_{k'}^{*} + l_k^{*} l_{k'})\} \tag{A5b}$$

According to eq A3, the total bond order for any pair of atoms, say a and b, in each member of an isomolecular family can be given in terms of the total bond order in the M_0 state plus or minus the partial bond orders from the HOMO and the LUMO.

The total BO for an a/b bond in M_0 is called $BO_0^{a/b}$. Let us define the partial BO's in the HOMO and LUMO orbitals[31] as

$$BO_H^{a/b} = \frac{(h_a h_{b'}^* + h_a^* h_{b'})}{2N_H} S_{ab} \tag{A6a}$$

and

$$BO_L^{a/b} = \frac{(l_a l_{b'}^* + l_a^* l_{b'})}{2N_L} S_{ab} \tag{A6b}$$

Thus, the electron numbers (matrix elements of the charge density operator) in eqs A3 are broken into charge densities on atoms and bond orders between them. Each is separately given by eq A3-like relationships, atom by atom and bond by bond. Thus, for the a/b bond in an isomolecular family we write

$$BO_{ST}^{a/b} = BO_0^{a/b} - BO_H^{a/b} + BO_L^{a/b} \tag{A7a}$$

$$BO_+^{a/b} = BO_0^{a/b} - BO_H^{a/b} \tag{A7b}$$

$$BO_-^{a/b} = BO_0^{a/b} + BO_L^{a/b} \tag{A7c}$$

or we recover the universal BO relationship for any given bond across a family, namely,

$$BO_{ST}^{a/b} = BO_+^{a/b} + BO_-^{a/b} - BO_0^{a/b} \tag{A8}$$

(the a/b version of eq 13). All BO's here are of course for an a/b bond length. This is common to all members of the family. They are *not* equilibrium bond orders $\overline{BO}^{a/b}$'s.

Appendix B

Inequalities for Any One-Electron Property across an Isomolecular Family ("State Ordering Rules"). Let us try to order with inequalities any general property A across any isomolecular family by expressing the HOMO and LUMO as a simple, normalized LCAO of two AOs, $|a\rangle$ and $|b\rangle$. The matrix elements of A in the AO basis shall be called A_{aa}, A_{bb}, and A_{ab}.

We know that

$$A_{ST} = A_0 - A_{HOMO} + A_{LUMO} \tag{B1a}$$

$$A_+ = A_0 - A_{HOMO} \tag{B1b}$$

$$A_- = A_0 + A_{LUMO} \tag{B1c}$$

in which the one-MO properties are just

$$A_{HOMO} = \frac{A_{aa} + A_{bb} + 2A_{ab}}{2(1 + S_{ab})} \tag{B2a}$$

$$A_{LUMO} = \frac{A_{aa} + A_{bb} - 2A_{ab}}{2(1 - S_{ab})} \tag{B2b}$$

Equations B1a−B1c in terms of the AO matrix elements are

$$A_{ST} = A_0 + \frac{2A_{ab} - (A_{aa} + A_{bb})S_{ab}}{S_{ab}^{\ 2} - 1} \tag{B3a}$$

$$A_+ = A_0 - \frac{(A_{aa} + 2A_{ab} + A_{bb})}{2(S_{ab} + 1)} \tag{B3b}$$

$$A_- = A_0 + \frac{(A_{aa} - 2A_{ab} + A_{bb})}{2(1 - S_{ab})} \tag{B3c}$$

We shall take $0 < S_{ab} < 1$ and consider two cases: (I) diagonal AO matrix elements dominate; (II) off-diagonal AO matrix elements dominate. Depending on the balance among A_{aa}, A_{bb}, and A_{ab} (even with all positive), we can get different answers.

(I) If for the force constants (or any Q-dependent property) we declare that the single atom matrix elements cannot contribute, then the general outcome is clear because now eqs B3a−B3c reduce to

$$A_{ST} \approx A_0 - \frac{2A_{ab}}{1 - S_{ab}^{\ 2}} \tag{B4a}$$

$$A_+ \approx A_0 - \frac{A_{ab}}{1 + S_{ab}} \tag{B4b}$$

$$A_- \approx A_0 - \frac{A_{ab}}{1 - S_{ab}} \tag{B4c}$$

For $A_{ab} > 0$ we can say that

$$A_{ST} < A_- < A_+ < A_0 \tag{B5}$$

$$\text{and the reverse would be true for } A_{ab} > 0 \tag{B6}$$

(II) If we declare that only the diagonal components dominate (and are relatively equal), then

$$A_{ST} \approx A_0 + \frac{(A_{aa} + A_{bb})S_{ab}}{1 - S_{ab}^{\ 2}} \tag{B7a}$$

$$A_+ \approx A_0 - \frac{A_{aa} + A_{bb}}{2(1 + S_{ab})} \tag{B7b}$$

$$A_- \approx A_0 + \frac{A_{aa} + A_{bb}}{2(1 - S_{ab})} \tag{B7c}$$

For $A_{aa} \approx A_{bb} > 0$ we then find that

$$A_- > A_{ST} > A_0 > A_+ \tag{B8}$$

For oppositely signed diagonal elements the inequalities in eq B8 would be reversed.

Let us analyze now the computational results from sections III.1−III.5 in the spirit of eqs B5 and B8, though these are strictly for one-electron properties. One may note that eq B5 is indeed obeyed for ethylene, CBDE, DPA, DVB, and N_2 while eq B8 holds for CO, C_2^{2-}, and N_2H_2. Equations B5 and B8 are thus valid for most of the species investigated, pointing to the respective dominance of nondiagonal and diagonal matrix elements of A in the AO basis. Interestingly, NO^+, CN^-, and O_2^{2+} do not obey either of these two equations and probably may be classified as an intermediate case, interplay of nondiagonal and diagonal matrix elements of A being of similar order.

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(31) The overlap integral, S_{ab}, is for the AO's appearing in the HOMO/LUMO at the ab bond. It is invariant over all species within any isomolecular family, since the electronic ASMO states are defined at a common set of nuclear coordinates (equilibrium or not) across the family.