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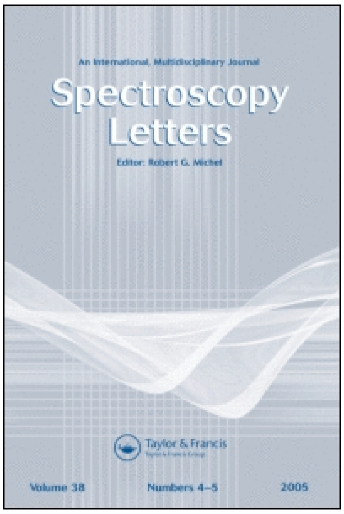

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Convenient Chemical Symbols to Illustrate Electronic Excited States

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Convenient Chemical Symbols to Illustrate Electronic Excited States

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Abstract: The problem of poor comprehension of electronic spectra by chemistry students in upper level undergraduate classes is addressed by consistent application of vector addition to both spin and angular momentum. Using the upgraded box-and-arrow diagrams, both atomic and molecular electronic states may be described without the use of advanced mathematics. Simple chemical symbols and formulas are suggested for molecular excited states that complement the existing physical/mathematical notation. Elements of a suitable classroom presentation are presented.

Keywords: Electronic spectra, spectroscopy term symbols, spin, student learning

INTRODUCTION

While teaching quantum mechanics and spectroscopy throughout my career, I noticed that many students have serious conceptual problems with the understanding and interpretation of electronic spectra. Based on my experience, the root of the problem is poor comprehension by students of electronic spins and the related *chemistry* of electronic excitation (i.e., how the electronic excitation affects the molecular structure). One of the reasons for this is that electronic structure, as a rather abstract topic, requires visualization for better

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understanding.[1] It is also well-known that any simple *physical* explanations of spin and angular momentum facilitate handling abstract mathematical term symbols.[2,3] Unfortunately, such explanations/visualizations are not consistently applied to this topic as a whole in the available textbooks.[4,5] For instance, textbooks usually cover spin multiplicity using the mathematical language of products of spin and spatial wavefunctions and do not adjust chemical formulas for electronic excited states. If these concepts are not intuitively understood, common symbols like S_0/S_1 and T_1 for the ground/first-excited singlet and triplet states, respectively, or symmetry-based term symbols of diatomics [${}^1\Sigma(\Pi)_\mathrm{g}$, ${}^1\Sigma(\Pi)_\mathrm{u}$, and ${}^3\Sigma(\Pi)_\mathrm{g}$], appear to be abstract in their bases. Then, simple figures depicting the energies of electronic and vibrational quantum levels of diatomic molecules, like those in Fig. 1, look incomprehensible.

There are legitimate problems with pictorial illustrations in spectroscopy; the pictures must be physically adequate and unambiguous. For instance, Noggle attempted the assignment of p^2 atomic states to box-and-arrow diagrams.[4] However, later Carlton pointed out that some of such pictures may not reflect a single quantum state and expressed doubt that representative and unambiguous pictures may be obtained to represent all of the atomic term symbols.[3]

This paper addresses this problem by consistent application of vector addition to both spin and angular momentum. Then, taking this approach one step further, I suggest symbols that adequately reflect the correct *physical* phenomena followed by upgrading the physical picture to the level of *chemistry*. Excited electronic states are different molecules than the corresponding ground states, with separate potential energy surfaces and unique chemistry. Thus, they should be given different chemical *formulas* adequately representing their electronic distribution (which, in turn, affects their physical

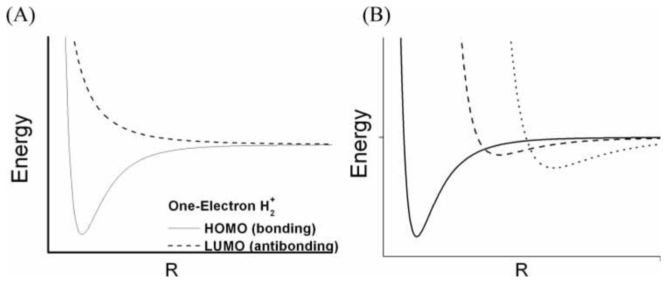


Figure 1. Qualitative energy sketches of ground and excited electronic states. (A) H_2^+, an example of a one-electron case. (B) A two-electron case with a relatively stable excited-state triplet (i.e., with degenerate π- or δ-orbitals, see the text). Solid line, a ground state singlet with two highest energy electrons on a bonding HOMO (A-B); dashed line, an excited state singlet with one electron promoted to an antibonding LUMO [A B$(\nearrow\swarrow)^*$]; dotted line, the corresponding triplet [A B$(\nearrow\nearrow)^*$].

and chemical properties). Combining box-and-arrow diagrams and Lewis structures with the analysis of vector addition, I came up with a set of simple chemical formulas to illustrate (but not to replace) the corresponding physical/mathematical notation, along with a suitable classroom presentation. My approach assumes familiarity with basic quantum mechanics but does not require any advanced mathematics.

SPIN MULTIPLICITY

I suggest drawing "leaned" rather than vertical arrows (↗, equivalent to ↖ in regard to z-axis vector projections; and ↙, equivalent to ↘) to depict electronic spins in box-and-arrow diagrams. This notation captures the mathematical significance of the spin vector addition and the physical essence of the rotating quantum particle's precession.[4] Traditional box-and-arrow diagrams show the sign of just m_s (the z projection of spin) for each electron as "spin up" or "spin down" (↑ and ↓). This is sufficient for the description of ground states of those atoms in which the electrons are paired within one orbital. However, for triplet and higher spin multiplicity states, two electrons do not occupy a single orbital; thus, the Pauli principle does not prevent their three possible spin vector combinations: ↗↗ (which is equivalent to ↖↖ in terms of the quantum numbers because it is the z projection that defines the quantum state), $M_s = +1$; ↘↘ (equivalent to ↙↙), $M_s = -1$; and ↗↘ (or ↖↙), $M_s = 0$ resulting in a triple-degenerate state with $S = 1$. The values of M_s and traditional box-and-arrow diagrams fail to distinguish between the $S = 0$ and $S = 1$ states for $M_s = 0$ (↑↓ and ↓↑), whereas the suggested symbols depict this difference adequately (↗↙ canceling the vectors for $S = 0$ and ↗↘ adding them up for $S = 1$, respectively). The latter are linear combinations of the former selecting the *extreme* (quantized) states out of a continuum of possible intermediate states.

ATOMIC SPECTROSCOPY: ADDITION OF ANGULAR MOMENTUM VECTORS

The combinatoric analysis of vector addition may be applied, in a similar way, to the *angular* momentum (quantum number L for multielectron systems) leading to modified box-and-arrow diagrams. To distinguish angular momentum from spin, a different style of thicker arrows will be used henceforth. For instance, let us consider the ground state of carbon, p^2. In general chemistry, students develop a misconception that the pairs of states shown in Figs. 2A, B, C, and in D, E, respectively, are degenerate. The commonly used Lewis dot structures of atoms only strengthen this misconception. Yet, three nondegenerate states exist in this system, $^3\mathrm{P}$, $^1\mathrm{D}$, and $^1\mathrm{S}$, the ground-state $^3\mathrm{P}$ further splitting at higher resolution into $^3\mathrm{P}_2$, $^3\mathrm{P}_1$, and $^3\mathrm{P}_0$ due to

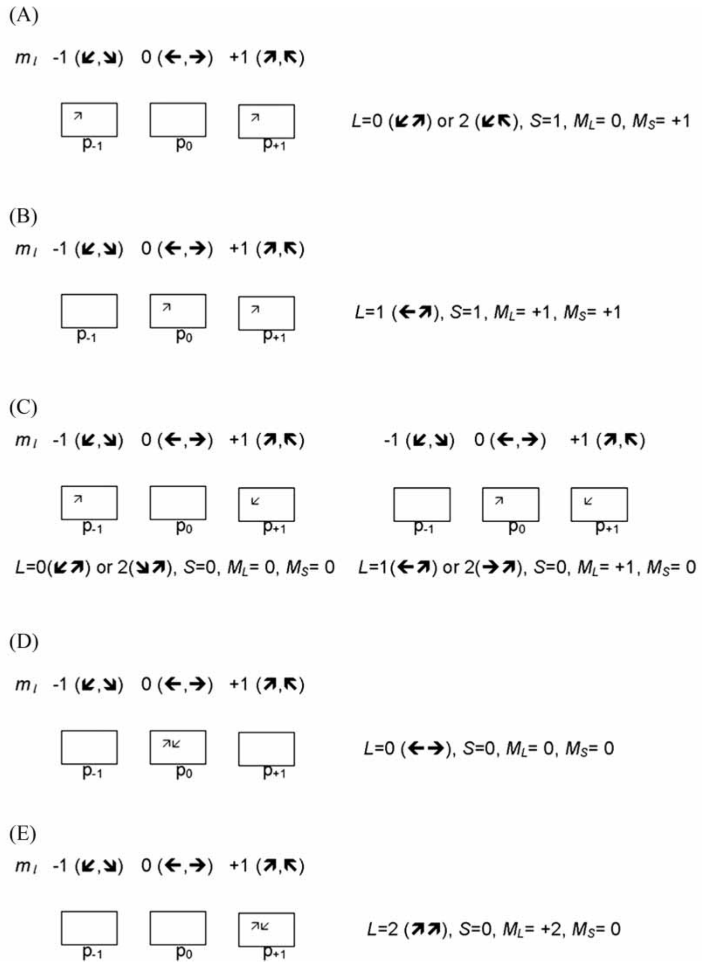


Figure 2. Box-and-arrow diagrams representative for the p^2 state. (A) ^{3}D or ^{3}S; both are nonexisting, see the text. Thus, this state is ^{3}P, a linear combination of ^{3}D and ^{3}S. (B) ^{3}P. (C). Left picture, ^{1}D or ^{1}S; right picture, ^{1}D or ^{1}P (the latter is nonexisting). (D) ^{1}S. (E) ^{1}D.

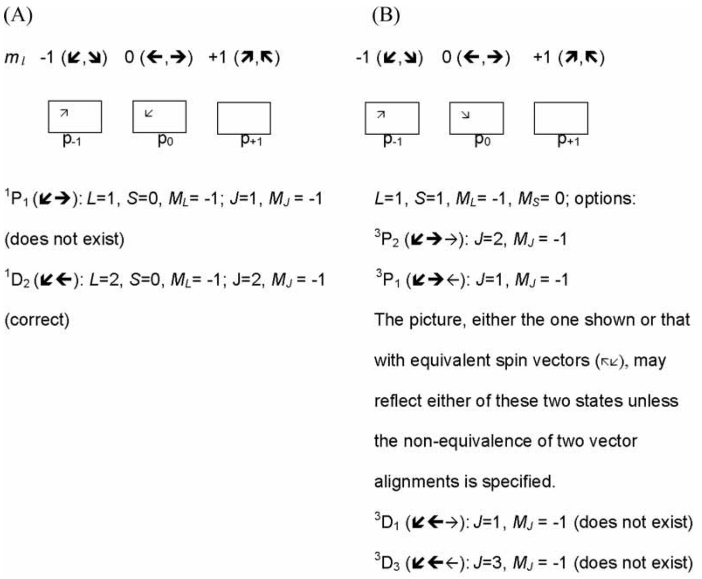
spin-orbit coupling.[4] I shall show that the combinatoric analysis of vector addition combined with the application of the Pauli principle in box-and-arrow diagrams leads to the correct assignment of term symbols.

Two p electrons with opposite values of m_l (Fig. 2A) may form either an S state ($L = 0$) if their angular momentum vectors cancel each other out (↗↙) or a D state ($L = 2$; $M_L = 0$) if they add up (↗↘). If one of the m_l values is zero and the other is not (Fig. 2B), the vectors either add or partially cancel each other (→↗ resulting in ↗ and ↖→ resulting in ↗), that is, yielding the vectors of the same projection but different length, D ($L = 2$) and P ($L = 1$) states, respectively. For either of these states, $M_L = \pm 1$; this value can also be obtained by the addition of vector projections (m_l). The singlet states corresponding with those in Figs. 2A, B are shown in Fig. 2C. For two *p* electrons located within the same orbital, there is no ambiguity in vector addition because either zeros or the projections of the same sign always add up (Figs. 2D and E, respectively). The resulting states are S and D, respectively; if this is D, the extreme M_L values ($\pm$ 2) are yielded because the angular momentum vectors are doubled.

Combining this consideration of angular momenta with the two possible spin states (singlet and triplet), ^{3}D, ^{1}D, ^{3}P, ^{1}P, ^{3}S, and ^{1}S term symbols can be envisioned. However, some of these states cannot exist because of quantum mechanical restrictions. Two electrons within three *p* orbitals can yield only 15 different configurations without violating the Pauli principle. $6 \times (6 - 1)/2! = 15$ distinct permutations are possible assuming $2 \times 3 = 6$ degrees of freedom for the first electron. Thus, there is no room for ^{3}D, which would require $3 \times 5 = 15$ states by itself (whereas some S and P states must exist, too, because *L* must take all of the integer values between $l_1 + l_2$ and $l_1 - l_2$). In addition, as shown by Noggle, accommodating $M_L = \pm 2$ for this triplet would require placing two unpaired electrons in one orbital, Fig. 2D, which is forbidden by the Pauli principle.[4] So, the only possible D state must be a five-degenerate ^{1}D (two like those in Fig. 2D, with M_L of ± 2, one like that in Fig. 2C, left picture, with $M_L = 0$, and two like those in Fig. 2C, right picture, with $M_L = \pm 1$).

For the remaining states, ^{3}P should be selected over ^{3}S to accommodate most of the remaining box-and-arrow diagrams. This term (^{3}P) has the lowest energy among the other p^2 terms (according to Hund's rule, due to maximum spin) and takes $3 \times 3 = 9$ states (some of its substates are shown in Figs. 2A, B). Now, only one remaining state out of 15 is left to account for. This eliminates ^{1}P and ^{3}S because either of them would require three degenerate states. Thus, the remaining state must be ^{1}S (Fig. 2D).

Each of these 15 states may be referred to an adequate box-and-arrow diagram.[4] Note, however, that sometimes one box-and-arrow diagram may be ascribed to two different terms (and vice versa), depending on how the two equivalent combinations of the precessing spin and angular momenta line up. Using the language of quantum mechanics, some of the suggested box-and-arrow diagrams are not eigenfunctions of operator L^2 as pointed out by Carlton.[3] A detailed explanation is provided in Fig. 3; Fig. 3A is unambiguous whereas Fig. 3B may be assigned to two substates with different values of *J*. Thus, this picture is, in fact, a linear combination of both quantum states. Similarly, Fig. 2A shows that one of the substates of ^{3}P originates from forbidden ^{3}S and ^{3}D, as their linear combination. However, if one of the box-and-arrow diagrams is assigned an unambiguous set of quantum numbers (e.g., Fig. 2D), this set cannot be applied to any



$^1P_1$ (⬋➔): L=1, S=0, M_L= -1; J=1, M_J = -1 (does not exist)

$^1D_2$ (⬋⬅): L=2, S=0, M_L= -1; J=2, M_J = -1 (correct)

L=1, S=1, M_L= -1, M_S= 0; options:

$^3P_2$ (⬋➔→): J=2, M_J = -1

$^3P_1$ (⬋➔←): J=1, M_J = -1

The picture, either the one shown or that with equivalent spin vectors (↖↙), may reflect either of these two states unless the non-equivalence of two vector alignments is specified.

$^3D_1$ (⬋⬅→): J=1, M_J = -1 (does not exist)

$^3D_3$ (⬋⬅←): J=3, M_J = -1 (does not exist)

Figure 3. Detailed vector addition analysis of two substates complementary to those shown in Figs. 2A–C (the subscript on the right denotes the total angular momentum, J). (A) One of the singlets; (B) one of the triplets.

other picture (so the left picture in Fig. 2C must correspond with ^{1}D because the alternative, ^{1}S, has been used).

Thus, modified box-and-arrow diagrams (pertaining to the atom of interest), combined with the angular momentum vector addition, may provide a tentative assignment of the general term symbols with the remaining ambiguity in assigning the L and J (total angular momentum) values to some of the pictures. To overcome this deficiency, the addition of both spin and angular momentum vectors may be depicted next to the atom of interest with arrows of different styles as in Fig. 3B. However, if the goal is just distinguishing between the ^{3}P, ^{1}S, and ^{1}D quasi-degenerate states, the representative pictures with *extreme* values of M_L shown in Figs. 2B, D, and E, respectively, would suffice.

To illustrate this method, the pictures reflecting three nondegenerate states for the p^3 electronic configuration ($6 \times (6-1)(6-2)/3! = 20$ states) are shown in Fig. 4. The spin multiplicity may be either 4 (an unambiguous case is, e.g., ↗↗↗, Fig. 4A; the others are ↙↙↙, ↗↘↗, and ↙↖↙) or 2 (↗↗↙ and ↗↙↙, e.g., Figs. 4B, C). Quadruplets of P, D, or F states cannot be accommodated because of large numbers of required substates (e.g., ^{4}D or ^{4}P in Fig. 4A). For the angular momentum, an F state would lead to a violation of the Pauli principle for the extreme cases of $M_L = \pm 2$ (three electrons would have to be in the right orbital

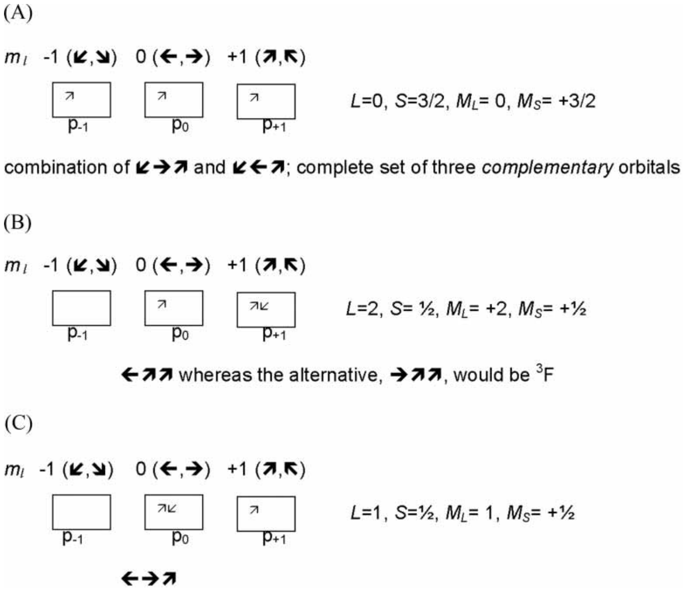


Figure 4. Box- and-arrow diagrams representative for the p^3 state. (A) ^{4}S, ground state (maximum spin). The alternative in L (^{4}D, with the L vector addition like ↘→↗) cannot be accommodated because it takes 20 substates. (B) ^{2}D. The alternative in L (^{2}F) cannot be accommodated because three electrons cannot occupy one orbital for the extreme case of $M_L = +3$. (C) ^{2}P. No ambiguity for this *extreme* value of M_L.

in Fig. 4B), so $L = 2$ is the maximum value. Eight (out of 10) most unambiguous pictures for ^{2}D state contain an electronic pair in the side boxes (Fig. 4B), whereas four (out of six) pictures for ^{2}P state have it in the middle (Fig. 4C). The rest of the ^{2}P and ^{2}D substates will be similar to that shown in Fig. 4A but with a *reduced* spin quantum number ($S = 1/2$); for example, ↙↗↗, ↗↗↙, ↗↙↙, and ↙↙↗.

It is noteworthy that the ground-state ^{4}S substates, for example, the one shown in Fig. 4A (all four with three p electrons occupying three *different* orbitals), represent true eigenfunctions. The addition of complementary orbitals in either filled or symmetrically half-filled electronic subshells (p, d, or f) yields a radially symmetric sphere with $L = 0$. However, three angular momentum vectors would not cancel each other out without considering a linear combination as shown in Fig. 4A. This contradiction is due to the uncertainty principle, which makes the x- and y-vector projections uncertain once its z-projection is specified. This is an inherent limitation of the suggested method.

The suggested approach can be expanded to the systems with different values of l such as transition metals or excited states (using different-size arrows for angular momentum vectors).

MOLECULAR SPECTROSCOPY: BONDING AND ANTIBONDING ORBITALS

Angular momentum vector addition in diatomic molecules is more straightforward than in atoms because the pertinent quantum number Λ is just a projection of the angular momentum vector on the principal axis of symmetry.[4] Thus, summing up the vector projections is sufficient; for example, for distinguishing between the $^1\Delta$ and $^1\Sigma$ excited states of O_2 (Fig. 5A), $\Lambda = +1 \pm 1$.[3] In ground states, σ, π and δ molecular orbitals can be distinguished based on their symmetry as it is done in general chemistry.

However, one additional problem, specific for molecules, needs to be addressed. In Lewis dot formulas, chemical bonds are traditionally represented as A:B or A-B. Even though this is adequate for most of the applications in chemistry, that is, *ground* electronic states (with a prominent exception of O_2, see below), such a representation of electrons is not sufficient for molecular spectroscopy (i.e., *excited* electronic states).

Simplified Lewis formulas, in addition to their failure to distinguish between the singlets and triplets, do not distinguish between the ground and low-lying excited electronic states differing in the location of one electron on a highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively.

Combining Lewis dot structures with modified box-and-arrow diagrams for the molecular orbital(s) of interest addresses both of these problems. To address the adequate electronic distribution, note that the lines depicting chemical bonds in traditional chemical formulas imply the overlap of atomic orbitals (AO) resulting in a lower energy molecular obritals (MO) compared with the original AOs (i.e., bonding orbitals). To show this explicitly, I suggest preceding the introduction of an A-B formula for the HOMO state with more realistic detailed schematics based on the correct electronic distribution of the two highest energy electrons. The suggested approach is applicable to the orbitals with any Λ (its extension from Σ orbitals considered in the next few cases requires no adjustment in symbols) and either diatomic or polyatomic molecules.

The essence of my approach can be illustrated using a one-electron case (e.g., H_2^+). In its ground state, the electron occupies the bonding HOMO. Because both of the atomic wavefunctions have the same sign with respect to the principal molecular axis, they overlap significantly between the atoms thus stabilizing the system by "gluing" the two nuclei together. The suggested detailed symbol

$$\underset{\mathrm{A\ \ B}}{\boxed{\ \nearrow\ }}$$

is, thus, adequate. Because the bond order is equal to one-half of the difference between the number of bonding and antibonding electrons, a simplified symbol of A−−B (with a "half-bond") is justified. Note that the dashed line showing this “half-bond” is elongated compared with the corresponding single bond thus reflecting the decrease of the amount of electronic “glue” connecting the nuclei. “Half-bonds” are known to be longer than single bonds based on spectroscopic measurements.[4]

However, if the electron in H_2^+ is promoted to its antibonding LUMO orbital, the atomic electronic wavefunctions have opposite signs, hence a nodal plane exists between the nuclei for the combined wavefunction

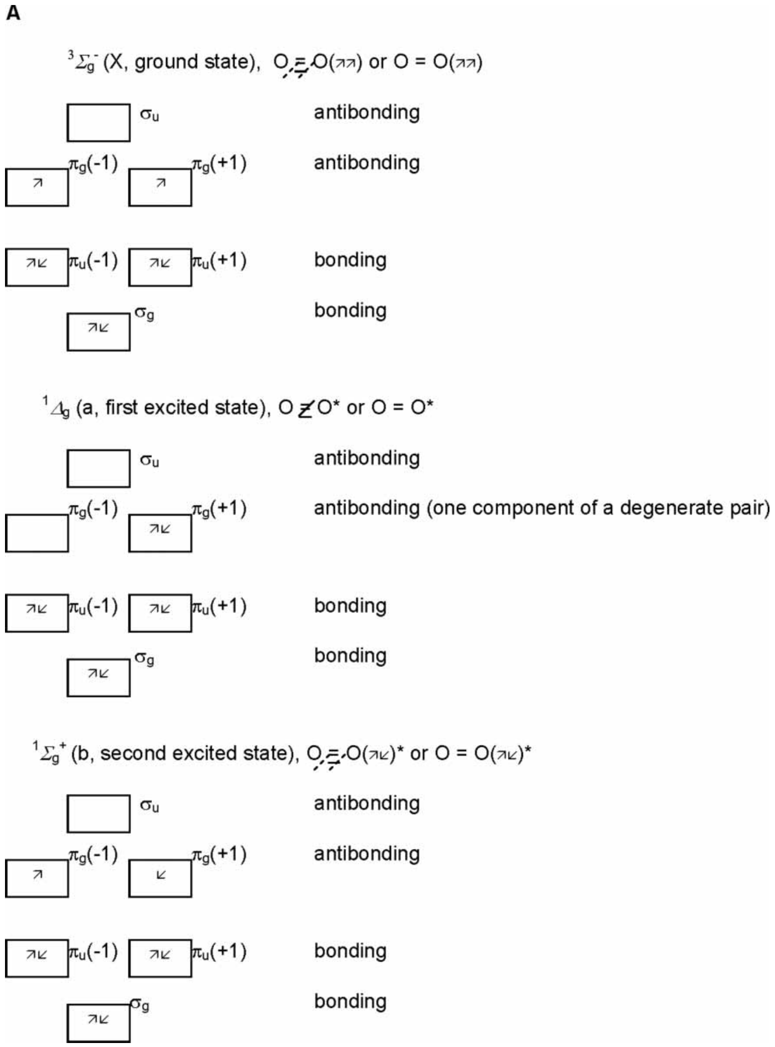


Figure 5A. Traditional box-and-arrow molecular orbital diagrams of the ground and low-lying excited states of N_2 (A) and O_2 (B). The Λ quantum number (± 1) is listed for π orbitals. (A) O_2.

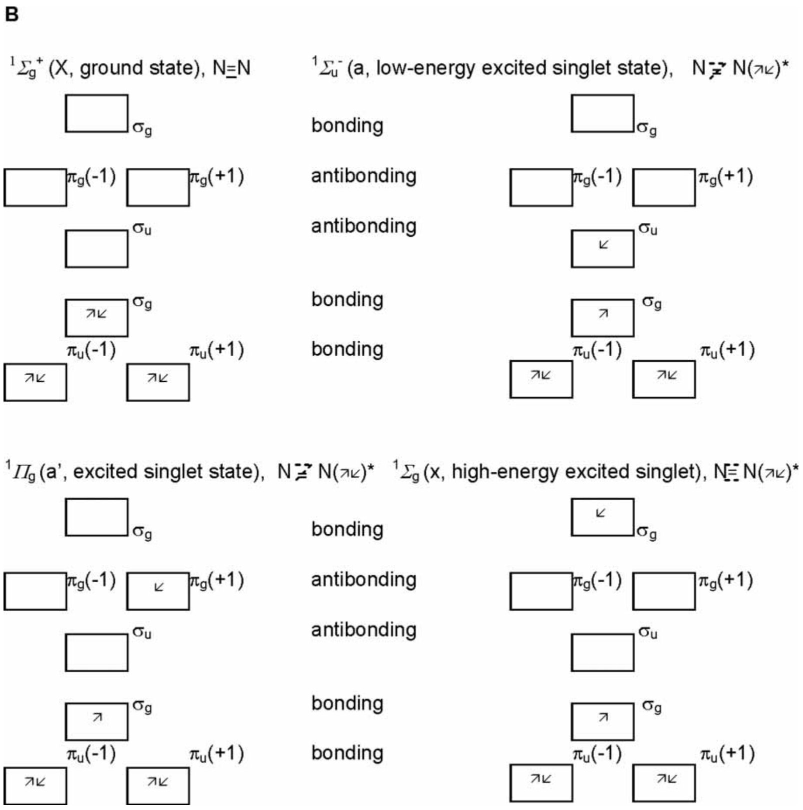
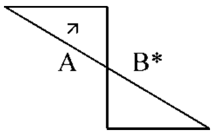
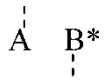


Figure 5B. N_2. Note that triplet rather than singlet excited states are observed in experimental spectra and that a number of other excited states exist because of similar energies for σ and π orbitals.[4]

(ungerade function). Therefore, the electronic density between the nuclei is low, and the resulting molecule would be thermodynamically unstable because of the conversion of a "half-bond" to the corresponding half-"antibond" as shown in Fig. 1A. If the original bonding orbital, regardless of its *L* quantum number, is represented as a rectangle, the resulting split into two antisymmetric lobes with a node in the center and two maxima of electronic density may be shown as



(the star denotes an excited electronic state; it has to be stressed that the electron is equally represented in each of the two parts of the orbital, which is not shown in the picture). In a simplified chemical formula, this can be shown as

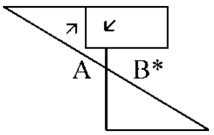


(i.e., with the "antibonds" sticking outward instead of connecting the atoms). This symbol will be revisited while considering the excited states of singlets.

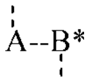
The ground state (^1X, S_0) of a closed-shell (singlet) molecule, for example, H_2 ($^1\Sigma_g{}^+$) could be represented as

showing the spin pairing of two electrons in one bonding molecular orbital. The suggested detailed formula reflects the fact that the HOMO occupied by two electrons is *bonding*, and, thus, the A-B simplified formula for this stable molecule is justified (with the understanding that placing the bonding electrons between the atoms does not necessarily reflect the *maximum* of electronic density in this area of the molecule).

For the first excited electronic state of a singlet molecule with the same spin multiplicity (A, S_1), electron spins still pair up, but one of the electrons occupies the next available molecular orbital, now LUMO instead of HOMO. The most interesting case in which the chemical structure is drastically altered is when the HOMO is bonding and LUMO is antibonding. As in the above-considered one-electron case (H_2^+), the electronic density between the nuclei is low, and so



is an appropriate detailed chemical symbol for this molecule. It reflects the real electronic distribution with the correct symmetry and illustrates the unpairing of two electrons located now on one HOMO and one LUMO orbital. A simplified formula, similar to that of H_2^+



can be used.

This formula can be improved if a symbol for an "antibond," A ⁄ B, is introduced. In this case, this is a "half-antibond" because it contains only one electron: A ⁄ B. Its combination with a "half-bond" provided by the nonexcited HOMO electron yields no bond, A⁄B* or simply A B*(↗↙), because one half-"antibond" tentatively offsets ("crosses out") one half-bond. The atoms are still held together because, due to a slower electronic speed in the space between the nuclei (i.e., greater "residence time" in this "gluing" region), the attraction "beats" repulsion for any two non-ionized atoms up to a certain distance corresponding with the bond length. This distance in the considered case of $A\ B(\nearrow\swarrow)^*$ is more consistent with intermolecular than with intramolecular interactions (with a shallow minimum) thus causing an increase of the interatomic distance compared with the corresponding ground state as shown in Fig. 1B.

If the LUMO is also a bonding orbital like HOMO, two "half-bonds" replace a single bond with a little change in the bond strength and length. The appropriate detailed and simplified chemical formulas are

$$\overset{\boxed{\nearrow}}{\underset{\boxed{\swarrow}}{A\ \ B^*}}$$

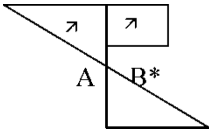
and $A\ \ B^*$ (denoting two "half-bonds"), respectively (e.g., N_2 in Fig. 5B, two top pictures). If both HOMO and LUMO are antibonding, the chemical change caused by electronic excitation is also minimal; the formulas of the ground and excited states are the same (barring the star), and so they can be distinguished only by their molecular term symbols.

So far, the low-lying molecular orbitals like HOMO-1, and so forth, were not shown because their electrons did not affect the essential physical properties (i.e., bond order and intermolecular distance) as much as the two highest energy electrons. If they do (e.g., for π orbitals), the stronger σ bond could be shown as a "stick" whereas the HOMO electrons are shown, as above, with their realistic most probable locations,

$$\overset{\boxed{\nearrow\swarrow}}{A—B}$$

yielding a double bond, A=B (or triple bond, Fig. 5B). The promotion of one of the HOMO electrons to an antibonding LUMO leaves only one σ bond in the excited singlet (or triplet) state because one more remaining half-bond (one-electron HOMO) becomes offset with one half-"antibond" (created by the electron promoted to LUMO) as shown earlier. Thus, the resulting $A\,\underset{\swarrow}{\overset{\nearrow}{-}}\,B(\nearrow\swarrow)^*$ [or $A—B(\nearrow\swarrow)^*$, if one half-bond is offset with one "half-antibond"] molecule is less stable (with a longer bond) than the ground state. It is much more stable, though (with a shorter internuclear distance), than its analog without a σ-bond, $A\ B(\nearrow\swarrow)^*$ considered earlier. The spins should be shown because the corresponding triplet may exist, too.

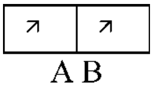
For the first triplet state (a, T_1) of a molecule like H_2, a symbol like



is similar to that of the corresponding excited singlet state but shows a non-zero total spin. This leads to an increased same-spin spatial separation (often called *Pauli repulsion*) leading to an even greater internuclear distance than in S_1 (Fig. 1B). The simplified formula is similar to that of the corresponding singlet, A B(↗↗)*, only with a greater interatomic distance and showing the extreme value of spin vectors' lineup to mark the triplet.

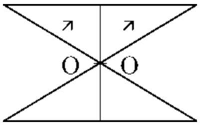
The triplet may be either more or less stable than the corresponding singlet depending on the order of molecular orbitals. For instance, the T_1 state of H_2 is unstable (unlike S_1). This system's energy does not have a minimum because the Pauli repulsion, combined with the promotion of one electron to an antibonding orbital of a much higher energy, tears this molecule apart. Thus, no phosphorescence is expected for singlets with no π or δ orbitals.

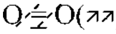
The opposite example of a *ground state* triplet (i.e., more stable than the corresponding singlet) is B_2 in which the HOMO is a double-degenerate bonding pπ orbital. The suitable detailed and simplified formulas for general chemical bonds like in B_2 are

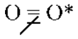
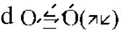


and A$\underline{-\,-}$B(↗↗), respectively (with two half-bonds; the overall bond order is 2). As Carlton showed earlier for a similar case of O_2, the triplet is more stable than the corresponding singlet because of the maximum spin rather than because of an increased spatial separation.[3] The spatial separation is the same for the singlet and triplet with the same Λ; the term *Pauli repulsion* should, thus, be used with caution. This analysis can be readily expanded to triplets and singlets of those excited states in which electrons are located on π and δ orbitals. Such excited states may exhibit phosphorescence because, once the orbitals can be spatially separated, triplets are more stable than the corresponding singlets as shown in Fig. 1B.

The most challenging ground-state molecule for any symbolic representation is O_2. The Lewis structure of its ground state, showing its triplet character by placing one unpaired electron on each of the oxygen atoms, necessitates a *single* bond (with a clear double violation of the octet rule), whereas the MO calculations yield the bond order of 2. The HOMO in O_2 is a double-degenerate antibonding orbital; these two electrons, because of Hund's rule and just like in B_2, tend to maintain the maximum spin and so they must occupy two separate orbitals to satisfy the Pauli principle[3] (Fig. 5A). Because these two π orbitals are spatially separated (perpendicular to each other), the Pauli repulsion is not fatal for this molecule; it just contributes to creating the maximum distance between the two highest energy electrons. A suitable two-dimensional approximation of the layout of two perpendicular π orbitals with two electrons could be shown as



The corresponding simplified formula is , or just $O = O(\nearrow\nearrow)$ reflecting the offsetting of one bond with two "half-antibonds" to yield the bond order of 2.

The suggested approach provides different chemical formulas for the two lowest energy excited states of O_2, $^1\Delta$ and $^1\Sigma$,  and , respectively (note that there is a full "antibond" in $^1\Delta$). The bond order is still 2 as in the ground state.

Not every higher lying excited state has a longer interatomic distance. One example is the ground-state triplet of O_2, $^3\Sigma$, compared with $^1\Delta$ in which no Pauli repulsion occurs but the bond order is the same (Fig. 5A). The former has the lowest energy, whereas the latter has the shortest interatomic distance between the two. Higher energy excited states have shorter bonds than lower-energy excited states when the electron is excited, first, to an antibonding LUMO and then to a bonding LUMO + 1 or LUMO + 2, and so forth,[5] for example, $^1\Sigma_u^-$ and $^1\Pi_g$ versus $^1\Sigma_g$ of N_2 (Fig. 5B). Using the above-considered symbols, these "exceptions" can be readily explained in terms of bond orders (see Fig. 5B).

One limitation of the suggested formulas, inherent to any simplified chemical bond presentation, is that the two depicted highest energy electrons appear to be localized around one particular bond. A more serious limitation is that, for instance, for any excited state of H_2 containing only *s*-electrons (e.g., 1*s*2*s*, 1*s*3*s*, and even double-excited 2*s*3*s*), the suggested approach yields the same formula, H-H* (thus, it is useful only for low-lying excited states). Finally, distinguishing some of the electronic states is possible only using the traditional term symbols, whereas the suggested approach yields the same formulas (as illustrated for $^1\Sigma_u^-$ and $^1\Pi_g$ of N_2 in Fig. 5B). This example stresses the fact that the suggested formulas are designed only as *illustrations* of term symbols because they, unlike the corresponding Lewis structures, are uniquely suited for showing both antibonding orbitals and triplet states and, unlike term symbols, are applicable to polyatomic molecules, regardless of their symmetry.

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