Calculation of the Lifetimes of Localized Electronic Vacancies in Cyclic Molecules*

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For a benzenelike ring of six carbon atoms the dissipation of localized electron vacancies of π and of σ symmetry is calculated. The vacancies are described by Wannier sums. The calculation yields lifetimes of localization of about 10^{-16} s in both cases. These values are shorter by two orders of magnitude than any period of molecular vibrations. Therefore such transiently localized vacancies, which can be caused by irradiation or by statistical fluctuations, will not destroy any bond in organic molecules.

1. Introduction

Further improvements of the resolving power of electron microscopes [1, 2] will offer the possibility of visualizing not only heavy atoms but also those of medium mass (C, N, O, P, etc.). The image of a molecule in such a microscope yields much more interesting results for biological chemistry than trying to resolve its structure by X-ray diffraction because the microscope will show an individual molecule, rather than just the average properties of many similar molecules. However, each directly imaged atom requires at least 3—6 elastically scattered electrons. Unfortunately, this occasions extensive radiation damage. Not only may *elastic* scattering processes transfer energy to the atomic nuclei, resulting in phonons or directly in a loss of hydrogen atoms by "knock-on" [3], but in biological molecules every elastically scattered electron is accompanied by about two *inelastically* scattered electrons, which cause much more damage. "Inelastically scattered" means that an incident electron has transferred energy to the *electrons* of the specimen to produce plasmons (as a collective excitation) or single-electron excitations.

Single-electron excitations seem to be most damaging. For example, a bond in the molecule may break if it loses a localized bonding electron. The worst case of a localized electron vacancy is a missing K electron, since a subsequent Auger effect causes the loss of two valence electrons nearby.

Stationary single-electron states in a molecule are described by molecular orbitals (MO). Their ψ-functions are generally not localized at single bonds but are spread throughout the molecule. Thus the contribution of each MO to a single bond is small, and the loss of an electron in one of those states will not break a bond. Nevertheless, two quite different possibilities exist in which the effect of a missing bonding electron is localized: (I) stationary MOs which are localized according to the molecular structure, and (II) nonstationary localizations resulting from local excitations or from statistical fluctuations.

(I) In a molecule having a distinctive site in its structure — for instance, a hetero atom among carbon atoms — much of the density of some MOs usually is localized around that point. If one of the localized MOs is among the highest occupied MOs, the loss of an electron anywhere in the molecule may result in loss of this localized electron, causing the molecule to break near that point [4]. This behaviour is well known from the molecular fragments recorded in mass spectrometry.

(II) The description of the molecule's electronic system by a set of stationary MOs is not the only possibility of using single-electron orbitals. Instead, when seeking localizations, one may calculate a set of Wannier sums as an equivalent description. These sums are linear combinations of stationary MOs, each sum accumulating most of its density at a distinct place in the molecule. Since the Wannier

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sums are composed of MOs of different energies, their localization is time-dependent. After some time their initially localized densities will spread over the molecule.

Although the whole set of Wannier sums is physically identical with the whole set of MOs, an empty Wannier orbital might cause a bond to break if its dissipation time is longer than about 10^{-14} s, which is the shortest period of phonons in organic materials. Yet when the dissipation time is much shorter, no excursion of the neighboring nuclei will result. Thus the stability of a given bond against breaking by localized loss of an electron can be investigated by calculating the lifetime of the corresponding Wannier sum.

The main topic of this study is to examine the lifetimes of localized electron vacancies, using as a model a simplified benzene molecule without its hydrogen atoms. The simplicity of the model makes the calculations more lucid. Due to the fully symmetrical structure any localizations of the electrons are nonstationary. Cyclic structures are quite common among organic molecules.

Benzene has both π and σ electrons. Comparison of both is of special interest because σ electrons might be presumed to show localizations of longer duration. This is because summation of the energies of localized σ bonds fairly well approximates their contribution to the molecule's binding energy, while the corresponding contribution of the π electrons can be obtained only by MO calculations. In addition, markedly different localization times would explain well the better resistance of molecules with π electrons against radiation damage — but no such differences appear in our calculation.

2. Atomic Orbitals and Bond Orbitals of Carbon in Benzene

Our aim is to construct the set of Wannier sums to describe localized electrons (or holes within the electronic system of a molecule) and to calculate the lifetimes of localization. This requires us first to calculate all occupied stationary MOs and their energies. As an approximation in this paper we construct these MOs as linear combinations of atomic orbitals (LCAO). Further on we consider only the carbon ring of benzene, not regarding the six hydrogen nuclei and their 12 bonding electrons. As atomic orbitals (AO) of the carbon atoms we use hydrogen-like functions.

$$\left.\begin{array}{rl} \psi_s = & (1 - Zr/2) \\ \psi_{px} = & Zx/2 \\ \psi_{py} = & Zy/2 \\ \psi_{pz} = & Zz/2 \end{array}\right\} \cdot \sqrt{\frac{Z^3}{8\pi}} \cdot e^{-Zr/2} \, , \; Z = 3.25 . \quad (1)$$

Here $r^2 = x^2 + y^2 + z^2$, and x, y, z are rectangular coordinates. For convenience all lengths and energies are given in Hartree units ($a_H = 0.529$ Å and $E_H = 27.21$ eV). The effective charge $Z = 3.25$ of the carbon nuclei accounts for the shielding of the nucleus by the inner electrons, according to Slater [5].

In the benzene molecule each carbon atom lies in a neighborhood of nearly trigonal symmetry. In such a symmetric field the first three functions of (1) combine to three hybrids of trigonal symmetry [6], leaving the ψ_{pz}-orbital for a π electron. In benzene therefore we use as AOs of all carbon atoms of *even* number (Figure 1):

$$\left.\begin{array}{l} \psi_{q1} = \sqrt{1/3}\,\psi_s - \sqrt{2/3}\,\psi_{px} \\ \psi_{q2} = \sqrt{1/3}\,\psi_s + \sqrt{2/3} \\ \qquad \cdot \{1/2\,\psi_{px} - \sqrt{3}/2\,\psi_{py}\} \\ \psi_{q3} = \sqrt{1/3}\,\psi_s + \sqrt{2/3} \\ \qquad \cdot \{1/2\,\psi_{px} + \sqrt{3}/2\,\psi_{py}\} \end{array}\right\} \sigma \text{ orbitals,}$$

$$\psi_{pz} \qquad\qquad\qquad\qquad\qquad \pi \text{ orbital.} \quad (2)$$

The trigonal field around each atom of *odd* number is rotated by 60° with respect to that of the adjacent even number. We define these as the hybrids
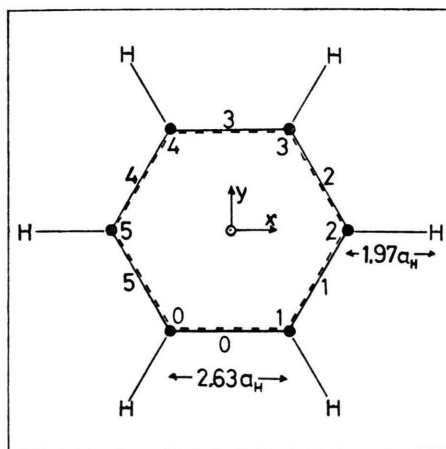

Fig. 1. Numbering of carbon atoms and their bonds in a benzene molecule.

$\psi_{\bar{q}1}$, $\psi_{\bar{q}2}$, $\psi_{\bar{q}3}$ by inverting the signs of ψ_{px} and ψ_{py} in (2). Each hybrid is axially symmetric and has one nodal surface, a hyperboloid surrounding the nucleus.

Because each hybrid's bonding capability is directional, it is useful to combine the appropriate hybrids of two adjacent atoms to form a *bond orbital*. There are two possibilities: the even combination results in a bonding orbital ψ^+ and the odd in a nonbonding orbital ψ^-. Taking bond 0 representative, we get

$$\psi_0^\pm = \frac{\psi_{q1}(\boldsymbol{r}_0) \pm \psi_{\bar{q}1}(\boldsymbol{r}_1)}{\sqrt{2}\{1 \pm \langle 0|1\rangle\}}. \qquad (3)$$

Here $\boldsymbol{r}_0$ and $\boldsymbol{r}_1$ are the radius vectors from the centers of atoms 0 and 1 respectively to the common coordinate point. The bonding orbital ψ^+ is scetched in Fig. 2 by contours of equal density. Having two electrons per σ bond, this even bonding orbital is the only one occupied and of further interest in this paper. The overlap integral is

$$\langle 0|1\rangle = \int_0^\infty \psi_{q1}(\boldsymbol{r}_0) \cdot \psi_{\bar{q}1}(\boldsymbol{r}_1) \, \mathrm{d}\tau = 0.7369. \qquad (4)$$

This is an integral of the two-center type, which can be evaluated analytically with elliptic coordinates. Its value comes remarkable close to unity.

This observation leads to two conclusions: *First*, the LCAO construction of both bond orbitals in (3) is only a poor approximation, as are all LCAO calculations for σ electrons using only the small set of AOs of Eq. (1), but ψ^+ is more accurate than ψ^- because of its larger denominator. For better approximations one would need to take into account higher hybrids of trigonal symmetry. *Second*, any LCAO calculation of σ bonds must evidently improve when bonding orbitals are employed instead of AOs. Consistent with this conclusion, the overlapp integrals between different bonding orbitals (Table 1) are quite small, even smaller than the overlap integrals between different π-AOs.

Table 1. Overlap integrals $\langle 0|\nu\rangle$ and overlap potentials V_ν.

Integral	π AOs	σ bonding orbitals	Potential	π AOs	σ bonding orbitals
$\langle 0|0\rangle$	1	1	V_0	-1.412	-1.588
$\langle 0|1\rangle$	0.4822	0.1468	V_1	-0.401	-0.303
$\langle 0|2\rangle$	0.1165	0.1211	V_2	-0.063	-0.226
$\langle 0|3\rangle$	0.0605	0.0789	V_3	-0.028	-0.158

3. Bloch Sums as Molecular Orbitals of the Carbon Hexagon and their Energies

The symmetry of σ orbitals is even and that of π orbitals is odd with respect to the molecular plane. Thus by symmetry no combination of elements of either group will overlap with those of the other group. Each can be treated separately.

When MOs are constructed as LCAOs in a cyclic molecule like benzene, these combinations, called Bloch sums, are fully determined by symmetry if just one AO contributes at each atom. For the π electrons $\psi_{pz}(\boldsymbol{r}_\nu)$ this means that their six MOs Ψ_m are given directly by (5a). The situation with the σ electrons' AOs is a little more complicated, but the benzene molecule's symmetry remains the same whether one examines the C-C bonds or the atoms (Figure 1). Thus Bloch sums can be used for the σ electrons too by inserting the six bonding orbitals ψ_ν^+ of (3) instead of the AOs $\psi(\boldsymbol{r}_\nu)$:

$$\Psi_m = N_m \cdot \sum_{\nu=0}^5 e^{i\pi m\nu/3} \cdot \psi(\boldsymbol{r}_\nu),$$
$$m = 0, \pm 1, \pm 2, 3. \qquad (5a)$$

The normalization factor is given by

$$N_m^{-2} = 6 \cdot \{1 + 2 \cdot \sum_{\nu=1}^2 \langle 0|\nu\rangle \cos(\pi m\nu/3)$$
$$+ (-1)^m \cdot \langle 0|3\rangle\}. \qquad (5b)$$

All overlap integrals $\langle 0|\nu\rangle$ contain only two-center-type integrations, which can be evaluated analytically with elliptic coordinates. The results are given in Table 1.

As Ψ_{+m} and Ψ_{-m} are complex conjugates of each other, they are degenerate in energy and have the same normalisation factor N_m. Further, one can replace the complex functions $\Psi_{\pm 1}$ and $\Psi_{\pm 2}$ by their real and imaginary components to get a set of real functions. This is done in Fig. 3, which shows all six σ-Bloch states of bonding orbitals, each occupied by two electrons. So there is an essential difference between π and σ electrons: all six σ-Bloch states are occupied, but the six π electrons will only occupy the three lower π-Bloch states Ψ_0, Ψ_1, and Ψ_{-1}.

The eigenenergies of the Bloch states are given by $E_m = \langle m|H|m\rangle$. From the Hamiltonian $H = H_0 + \sum_\nu V(r_\nu)$ we can separate out the Hamiltonian H_0 of a single carbon atom or of a C-C bond in the cases of π or σ orbitals respectively. As a model of the atomic potential $V(r)$ we use a combination of a
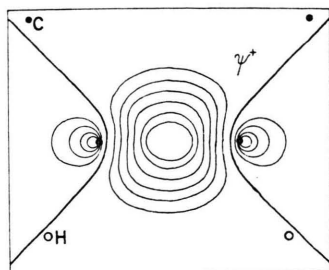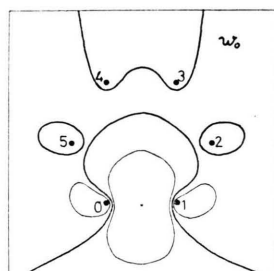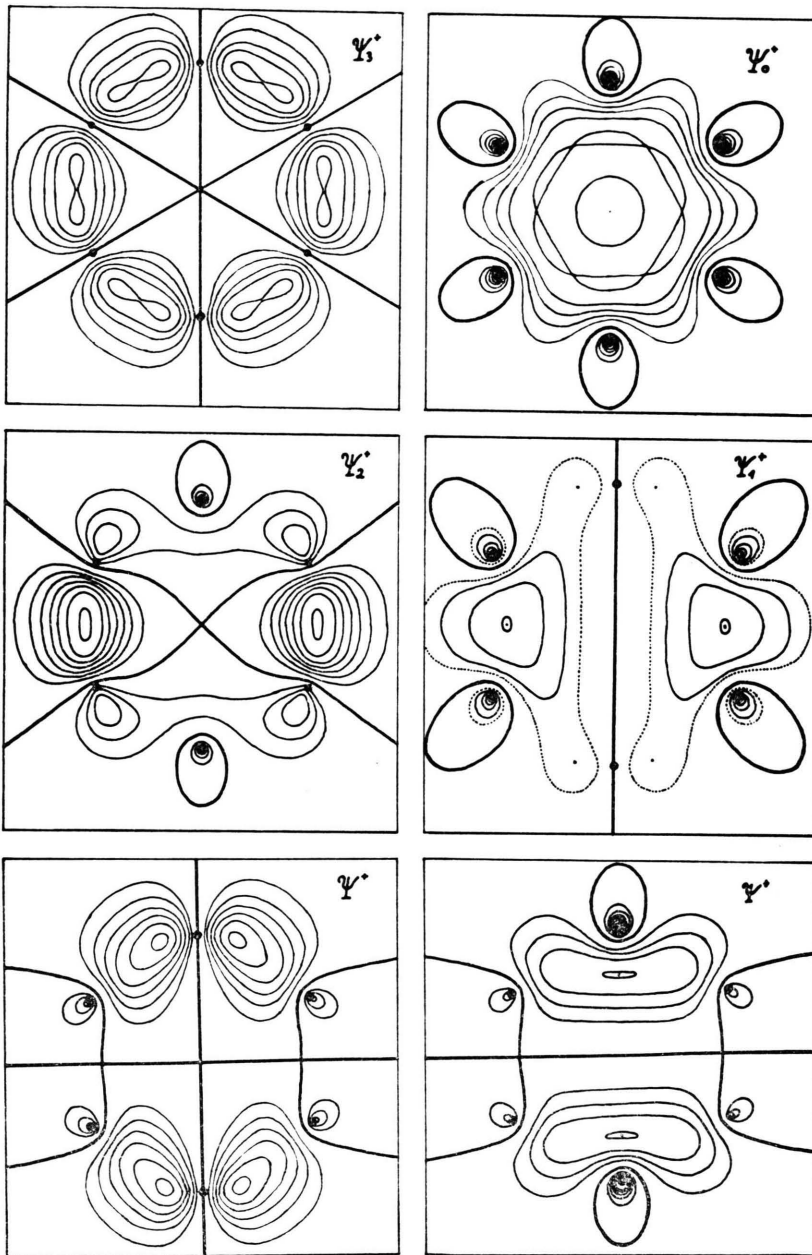
Fig. 2. Cross-section through the bonding orbital ψ^+.

Fig. 4. Contours of equal charge density for the Wannier sum w_{00} of σ symmetry. The heavy lines indicate the section through the nodal surfaces.

Fig. 3. Distribution of charge within all six Bloch sums Ψ_m of bonding orbitals.

Coulomb potential (representing an atom which has lost one of its electrons to the MO) and a Wentzel potential (representing the potential of an atomic nucleus shielded by the other electrons) [7]:

$$V(r) = -(1 + 4.25 \cdot e^{-1\,36r})/r. \qquad (6)$$

This formula omits a short-range term that would supplement the charge to the true value $Z = 6$ of the carbon nucleus, though it has little effect in a valence-electron calculation.

Now the Bloch energies can be written:

$$E_m = E_u + \frac{V_0 + 2\,V_1 \cos(\pi m/3) + 2\,V_2 \cos(2\,\pi m/3) + (-1)^m\,V_3}{1 + 2\langle 0|1\rangle \cos(\pi m/3) + 2\langle 0|2\rangle \cos(2\,\pi m/3) + (-1)^m\langle 0|3\rangle}. \qquad (7)$$

The denominator contains the square of the normalisation factor in (5b). We define E_u to be the undisturbed eigenenergy of the AO ψ_{pz} of a free carbon atom *or* of the bonding orbital ψ^+ in the potential of two neighboring carbon atoms. Here $V_\nu = \langle 0 | \sum_\mu V(r_\mu) | \nu \rangle$ contains a summation over $\mu = 1, \ldots, 5$ for π-AOs, but for bonding orbitals this sum should cover only $\mu = 2, \ldots, 5$.

In this paper we use only a basic LCAO approximation of the σ bonding orbitals ψ^+. When we express ψ^+ by the atomic hybrids ψ_q of (3), it therefore is more accurate to define E_u in (7) as the eigenenergy of ψ_q in the potential of a *single* carbon atom. Now each integral containing bonding orbitals must be reduced to a sum of appropriate integrals containing atomic hybrids.

The overlap potentials V_ν in (7) generally consist of three-center-type integrals, which can only be evaluated numerically. Elliptic coordinates centered in both AOs are helpful again in creating a dense net of integration points near the axis, and fewer points outside, where the product of both AOs becomes small. Only when two of the three centers coincide does the integral degenerate into a two-center type that can be evaluated analytically. Thus analytical integrations may serve to test the accuracy of the numerical integrations. The results are given in Table 1.

From (7) and the values of Table 1 we calculate the Bloch energies of π and σ electrons. These are listed in Table 2 with the atomic eigenenergies E_u subtracted. The Bloch energies of benzene's K electrons are taken from Niessen et al [8]. As our approximation of bonding orbitals is poor and the calculation is limited to the C_6 ring of benzene, the energies of the σ electrons can only be deemed very approximate. Yet, as our purpose is to calculate the lifetimes of localizations, only the amount of splitting of the energies within each group is of further interest.

Table 2. Bloch energies E_m-E_u from Eq. (7) in atomic units. K values are from [11].

Bloch state	π electrons	σ electrons	K electrons
Ψ_0	−1.497	−1.736	−11.2602
Ψ_1	−1.439	−1.592	−11.2597
Ψ_2	−1.332	−1.501	−11.2586
Ψ_3	−1.269	−1.466	−11.2580

4. Wannier Sums as Localized Molecular Orbitals

Using Bloch sums as the stationary MOs of cyclic molecules makes it quite easy to form Wannier sums w_ν [9], each of which is the MO maximally localized at the AO or at the bonding orbital $\psi(r_\nu)$ of (5a):

$$w_\nu(r, t) = 6^{-1/2} \cdot \sum_{m=-2}^{3} e^{-i\pi m \nu/3} \cdot \Psi_m(r) \cdot e^{-itE_m/\hbar} . \tag{8a}$$

All 12 time-dependent Wannier sums of σ and π symmetry are mutually orthonormal, just as the Bloch sums are. The backtransformation looks quite analogous:

$$\Psi_m(r) = 6^{-1/2} \cdot \sum_{\nu=0}^{5} e^{i\pi m \nu/3} \cdot w_{\nu 0} ,$$
$$w_{\nu 0} = w_\nu(r, t = 0) . \tag{8b}$$

Inserting (8b) into (8a), we can express the time-dependent Wannier sums $w_\nu(r,t)$ by a combination of Wannier sums $w_{\nu 0}$ for maximum localization:

$$w_\nu(r, t) = 6^{-1} \cdot \sum_{\mu=0}^{5} w_{\mu 0} \cdot \sum_{m=-2}^{3} e^{i\pi m(\mu - \nu)/3} \cdot e^{-itE_m/\hbar} . \tag{8c}$$

At $t = 0$ the summation over m yields zero for $\mu \neq \nu$. Thus (8c) describes an electron initially localized at $w_{\nu 0}$ but spreading over the entire set, losing its localization for $t > 0$.

Of course, the Wannier sums of (8c) can be used instead to describe an initially localized hole within the otherwise complete set of six orbitals. Figure 4 shows the Wannier sum w_{00}, which is localized on bond 0. Though it looks quite different at first glance from the bonding orbital ψ_0^+ of Fig. 2, their similarity is revealed by comparing the spatial charge distribution rather than the nodal surfaces of the two functions. The overlap integral between a Wannier sum $w_{\nu 0}$ and the corresponding bonding orbital ψ_ν^+ of the σ system,

$$\int_0^\infty w_{\nu 0} \, \psi_\nu^+ \, d\tau = 0.9917 ,$$

is quite close to unity. For comparison, the corresponding integral of the π system yields

$$\int_0^\infty w_{\nu 0} \, \psi_{pz}(r_\nu) \, d\tau = 0.9842 ,$$

which is only a little smaller. Thus in each case there is not much difference initially between a

Wannier sum $w_\nu(t=0)$ and the corresponding atomic or bonding orbital.

Our interest in the time-dependency of (8a) or (8c) is to learn how long a localization will last. To do so, we define the lifetime $T_{1/2}$ of localization, after which in (8c) the absolute value of the coefficient of $w_{\mu 0}$ equals $2^{-1/2}$, i.e., in a period of $T_{1/2}$ the bond has decayed to half of its initial density. The results are given in Table 3. Compared with the shortest period of vibrations in organic materials, 10^{-14}s, these times are short enough to exclude the possibility of breaking a bond by localized absence of a bonding electron. Using the values of Niessen et al. (Table 2) for the K electrons of benzene, we get $T_{1/2} = 2.5 \cdot 10^{-14}$s. Even this time is of the same order of magnitude as the shortest molecular vibrations. But nevertheless a K-shell defect is a local event in the molecule because within $3 \cdot 10^{-16}$s it will decay by Auger effect [7] to yield two valence electron vacancies nearby.

The time of localization is similar for π and σ electrons, but there is an important difference between the two systems when we consider a localized *hole*. The 12 electrons of the ring's σ system occupy all six Bloch states, whereas the six π electrons only occupy Ψ_0, Ψ_1, Ψ_{-1}. So $w_\nu(r,t)$ of (8c) can be used to describe a localized hole within the σ system but not within the π system.

Upon forming localized orbitals from only the three occupied MOs of the π electrons, we get unifrequent Wannier sums:

$$p_\nu(r,t) = 3^{-1/2} \cdot \sum_{m=-1}^{1} e^{-i\pi m \nu/3} \cdot e^{-itE_m/\hbar} \cdot \Psi_m(r)$$

$$= 18^{-1/2} \cdot \sum_{\mu=0}^{5} w_{\mu 0} \cdot \sum_{m=-1}^{1} e^{i\pi m(\mu-\nu)/3}$$

$$\cdot e^{-itE_m/\hbar}. \tag{9}$$

A unifrequent sum contains only MOs of two different energies E_0 and E_1, so that p_ν oscillates with only one frequency $\omega = (E_1 - E_0)/\hbar$. The term p_ν is taken to indicate the connection of this oscillation

with plasmons because its charge distribution amounts to an oscillating dipole of molecular size, strongly coupled to electromagnetic radiation. The index ν may take any value from 0 to 5, so as to define the locus of maximum density. But only the three odd *or* the three even values of ν define an orthonormal set of Wannier sums. The set

$$\{p_0(r,t),\ p_2(r,t),\ p_4(r,t)\},$$

for instance, describes the same electronic system as

$$\{\Psi_0(r),\ \Psi_1(r),\ \Psi_{-1}(r)\}.$$

Again the charge distribution of an entire set of p_ν is uniform within the molecule and does not oscillate.

Analogously to (9) we may form unifrequent Wannier sums in the π system by combining an occupied and empty Bloch orbital. The charge distribution of such a Wannier sum contains the transition element between both Bloch orbitals and will result in an oscillating dipole again of molecular size if the two constituent Bloch orbitals have subsequent indices. (Otherwise one gets quadrupoles or sextupoles.)

As we have presented only a simple a priori calculation of the benzene molecule, omitting all hydrogen atoms and their bonding electrons, it is of interest to compare our results with those obtained from CNDO/2 [10] and MINDO/3 [11] for the entire molecule C_6H_6 (Table 3). All 12 electrons bonding the hydrogen atoms have σ symmetry. Thus, when dealing with the entire molecule, we find *two* different MOs having the same cyclic symmetry as each of the six σ-Bloch sums of our calculation. To get a Wannier sum of maximum localization at one of the C-C bonds, one must combine all but one of these MOs. Both CNDO and MINDO calculations give somewhat shorter, though differing lifetimes. Nevertheless, all three methods yield lifetimes of the same order of magnitude.

5. Conclusions

Our calculations employing the simplified model of a benzene molecule have yielded some results generally valid for organic molecules.

Because of the strong overlap of directional hybrids from one atom to the next, bonding orbitals have the same importance in a molecule's σ system as do AOs in the π system. From the small overlap

Table 3. Time of localization of an electron in a π-AO or σ bonding orbital, calculated from the values of Table 2 and from results of CNDO/2 and MINDO/3 computations of the entire molecule C_6H_6. All times are $\times 10^{-16}$ s.

This calculation	CNDO/2	MINDO/3	Symmetry
2.4	0.87	0.80	π
2.2	0.91	0.53	σ

between bonding orbitals in different bonds, it seems obvious that the linear combinations of bonding orbitals should yield better results than the usual LCAO methods. This circumstance also explains the effectiveness of calculating binding energies just by summing up localized σ bonds.

In highly symmetrical molecules such as benzene, both π and σ electrons are delocalized, and any localization of an electron vacancy is so brief that it cannot destroy a bond. Moreover, a hole within the three occupied Bloch states of π electrons cannot be localized to the same extent as a hole within the otherwise complete set of six σ orbitals. Thus the better resistance against radiation damage by molecules having π electrons cannot be explained by a difference in the times of localization of vacancies.

Nevertheless there is a good explanation of this effect. Because only half of the Bloch states of π electrons are occupied, single unifrequent Wannier sums p_ν of Eq. (9) can exist within the complete π system without being compensated by the two others. As each p_ν represents an oscillating electric dipole of molecular size, its strong coupling with electromagnetic radiation gives rise to plasmons and single π excitations of *short* lifetimes. Thus the π system shields its own rigid σ system and that of neighboring molecules.

MOs of less symmetrical molecules cannot be constructed just by symmetry considerations. Moreover, combining their stationary MOs to localized Wannier sums is more complicated. Yet all our arguments remain valid. One significant difference exists, however, between molecules of high and of arbitrary symmetry. In less symmetric molecules some of the stationary MOs can be quite localized or some Wannier sums can exist with quite long lifetimes of localization. Both situations can result in breaking of certain bonds after electronic excitation.

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