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On the Rules of Scheibe*, **

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Scheibe's rules state that ionization potentials of first and higher excited states in molecules are approximately constant and hydrogen-atom-like. A simple explanation is given emphasizing the atomic nature of this effect. The analysis is based on a partitioning of space into nonoverlapping regions and the diffuse character of local charge distributions in singly-occupied antibonding MO's. The existence of bonding MO's in small molecules like H_2 is briefly discussed.

Die Scheibeschen Regeln sagen aus, daß die Ionisierungsenergien angeregter Zustände in Molekülen konstant und wasserstoffatomähnlich sind. Wir geben eine einfache Erklärung, die die atomare Natur dieses Effektes betont. Die Ableitung basiert auf Raumaufteilung in nichtüberlappende Gebiete und diffusem Charakter der lokalen Ladungsverteilung in einfach besetzten antibindenden MO's. Auf das Vorkommen bindender MO's in kleinen Molekülen wie H_2 wird kurz eingegangen.

Les règles de Scheibe affirment que les potentiels d'ionisation du premier état excité et des états excités plus élevés des molécules sont approximativement constants et semblables à ceux de l'atome d'hydrogène. On fournit une explication simple en insistant sur la nature atomique de cet effet. L'analyse est fondée sur une division de l'espace en régions disjointes et sur le caractère diffus des distributions de charge locale dans les orbitales moléculaires antiliantes simplement occupées. L'existence d'orbitales moléculaires liantes dans des petites molécules comme H_2 est brièvement discutée.

1. Introduction

Almost twenty years ago, Scheibe and coworkers [1] discovered in an investigation of a large number of molecules that the difference between first-excited state energy and ionization limit is approximately constant. The effect was also studied for second-, third- and some fourth-excited states. Scheibe tentatively assigned them as $2p\pi, 3p\pi, 4p\pi$, etc., and compared their relative energies with the excited states of the hydrogen atom.

A theoretical discussion in terms of Hückel theory was given by Hartmann [2]. He found that an admixture of $3p\pi$ atomic orbitals to the usual $2p\pi$ orbitals could explain Scheibe's findings. Later Kollaard and Colpa [3] suggested that an explanation based solely on $2p\pi$ orbitals was possible.

Both of these explanations were embedded in concepts of the old semiempirical methods, with Slater exponents for AO's and a common basis set for both ground and excited states. The following explanation, involving a new concept of antibonding orbitals, may be more realistic.

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2. Derivation

For convenience we study the effect in a simple hydrocarbon which is representative for π-electron systems: ethylene. In the π-electron approximation [4], the ground state is represented by a doubly-occupied bonding MO ϕ_0, the first-excited state by a singly-occupied MO ϕ_0 and a singly-occupied antibonding MO ϕ_1, and the ionized state by a singly-occupied MO ϕ_0. Contrary to previous approaches, we shall compare first-excited state and ionized state directly, i.e., without direct reference to the ground state.

The total wavefunctions of the two states are

$$\begin{aligned} {}^{1,3}\Psi &= \tfrac{1}{2}\{(\phi_0\bar{\phi}_1) \mp (\bar{\phi}_0\phi_1)\} \\ {}^{2}\Psi &= \phi_0 \end{aligned} \tag{1}$$

and their energies are

$$\begin{aligned} {}^{1,3}E &= {}^{1,3}\varepsilon_0^{\text{core}} + {}^{1,3}V_{\text{nuc}} + {}^{1,3}\varepsilon_1 \\ {}^{2}E &= {}^{2}\varepsilon_0^{\text{core}} + {}^{2}V_{\text{nuc}}\,. \end{aligned} \tag{2}$$

$\varepsilon_0^{\text{core}}$ is the core energy of the electron in the bonding orbital, V_{nuc} is the interaction energy of the framework and ε_1 is the SCF energy of the electron in the antibonding orbital. It is reasonable to assume that the removal of an electron from a singly-occupied antibonding orbital does not change very much the sum of core attraction and framework interaction of the remaining electrons. Thus the energy difference ΔE between first-excited and ionized state is equal to the SCF energy of the electron in the antibonding orbital.

$$\Delta E = \varepsilon_1\,. \tag{3}$$

This means that we assume Koopman's theorem to be valid for excited states.

Let us now proceed to some more specific considerations. The MO's ϕ may be represented by a sum of cut-off AO's [5, 6] defined in three nonoverlapping

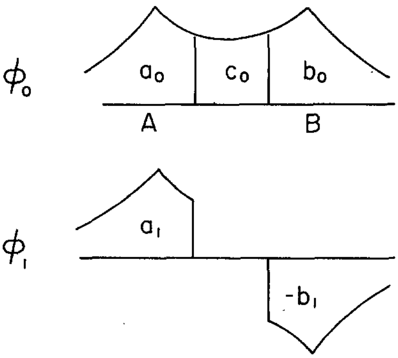

Fig. 1. Partitioning of bonding orbital ϕ_0 and antibonding orbital ϕ_1 in three nonoverlapping parts a, b, c for 1*s* orbitals

regions of space: two atomic and one bonding region.

$$\begin{aligned}\phi_0 &= (2+\langle c_0|c_0\rangle)^{-1/2}(a_0+b_0+c_0)\\ \phi_1 &= 2^{-1/2}(a_1-b_1)\,.\end{aligned}\tag{4}$$

For 1*s* orbitals these functions are schematically presented in Fig. 1; a and b are renormalized and represent the atomic regions, c_0 is continuous with a_0 and b_0 on the boundary surfaces and represents the bonding region. Questions concerning the discontinuity in ϕ_1 are discussed elsewhere [6]. With these assumptions and a partitioning of the SCF energy into core attraction and electron interaction, the energy difference ΔE becomes

$$\begin{aligned}\Delta E &= {}^{1,3}E-{}^{2}E\\ &= \varepsilon_1^{\text{core}}+J\pm K\\ &= \langle\phi_1|T-\frac{Z_{\text{eff}}}{r_a}-\frac{Z_{\text{eff}}}{r_b}|\phi_1\rangle\\ &\quad +\langle\phi_0\phi_0|\phi_1\phi_1\rangle\pm\langle\phi_0\phi_1|\phi_0\phi_1\rangle\\ &= \langle a_1|T-\frac{Z_{\text{eff}}}{r_a}-\frac{Z_{\text{eff}}}{r_b}|a_1\rangle\\ &\quad +\langle\phi_0\phi_0|a_1a_1\rangle\pm\langle\phi_0a_1|\phi_0a_1\rangle\mp\langle\phi_0a_1|\phi_0b_1\rangle\,.\end{aligned}\tag{5}$$

If the dimensions of the charge cloud of the antibonding orbital become large compared to the internuclear distance, the effective charge Z_{eff} will approach unity. The difference of exchange integrals $\langle\phi_0a_1|\phi_0a_1\rangle$ and $\langle\phi_0a_1|\phi_0b_1\rangle$ will become negligibly small and the Coulomb repulsion integral $\langle\phi_0\phi_0|a_1a_1\rangle$ will approximately cancel the nuclear attraction term $\langle a_1|-\frac{Z_{\text{eff}}}{r_b}|a_1\rangle$. The final expression for ΔE then takes the form

$$\Delta E=\langle a_1|T-\frac{1}{r_a}|a_1\rangle\,.\tag{6}$$

This formula is of course approximate, but it should describe the situation fairly accurately.

Because of its cut-off character, a_1 cannot be an exact eigenfunction of the hydrogen atom Hamiltonian. But since it is normalized, the integral (6) should come close to a hydrogen atom energy if a proper type of orbital with a hydrogen atom exponent is chosen. This would be in the case of ethylene a $2p\pi$ orbital with $\zeta=1/2$. This is exactly what Scheibe found in his investigation. Hence we expect from experiment that an atomic exponent of 0.5 in antibonding $2p\pi$ orbitals would be more appropriate than Slater exponents which are about three times larger. This conclusion is in agreement with a calculation by Huzinaga [7], who found $\zeta=0.4$ most appropriate for the antibonding orbital in ethylene. His grid of $\Delta\zeta=0.2$ was too coarse for greater accuracy.

Scheibe also collected data for several molecules, e.g., H_2 and Li_2, in which the situation is completely different from ethylene. In the case of H_2, the first excited Π state is obtained by the promotion of an electron from a bonding σ MO to a bonding π MO. It is the second excited Π state which contains an antibonding π MO. These two states labeled Π_u and Π_g have been extensively studied by Jug *et al.* [8]. It was found that in the LCAO description the π_u orbital is described mainly by a linear combination of $2p\pi$ AO's with exponents $\zeta = 0.442$ for $^1\Pi_u$ and $\zeta = 0.562$ for $^3\Pi_u$ at 2 Bohr. The SCF energy of the former state is slightly higher and of the latter slightly lower than the energy of the first-excited state of the hydrogen atom. Most remarkable is the Π_g state, where the π_g orbital at 2 Bohr is a linear combination of 99% of $2p\pi$ orbitals with exponents $\zeta = 0.245$ and 1% of $3d\pi$ orbitals. The SCF energy equals the $3d$-energy of the hydrogen atom to three figures. The singlet-triplet splitting is negligibly small. Here Scheibe's rule describes the situation better than in the Π_u states.

There are some questions which are still unanswered. One concerns the practical definition of the bonding region, the other the explicit form of the atomic basis functions. Some discussion can be found elsewhere [6]. However, the mathematical evaluation offers difficulty and the consequences of truncation and discontinuous functions are not yet completely explored.

3. Conclusion

We have seen that Scheibe's rules can be explained on the basis of atomic considerations. Two different situations exist in molecules, which are distinguished by the bonding and antibonding character of the highest singly occupied MO. The two cases are typified by H_2 and ethylene. In both cases the expection values of the charge distribution of the π orbital perpendicular to the molecular axis is large compared to the internuclear distance. For example, in H_2 it yields (at an internuclear distance of 2 Bohr) for $^1\Pi_u$, $\langle \varrho_\pi^2 \rangle^{1/2} = 5.6$ Bohr and for $^1\Pi_g$, $\langle \varrho_\pi^2 \rangle^{1/2} = 8.8$ Bohr. This allows us to characterize the situation as nearly atomic. It is the expansion of the main LCAO orbitals rather than the admixture of higher AO's which is responsible for the effect. For larger polyatomic molecules, we expect the situation to be ethylene-like, i.e., characterized by local antibonding expansions upon excitation.

Here we have invoked a picture where the basis functions entering the antibonding orbitals are atomic orbitals which are separated by a nonbonding region. We promote the idea that antibonding orbitals are almost nonbonding. A calculation on the antibonding orbital of $^1\Pi_g$ in H_2 substantiates this [9]. We point out that this view of the antibonding orbital has consequences for the parametrization of semi-empirical methods. The energy difference between bonding and antibonding orbitals should be set equal to β rather than 2β.

Finally, Scheibe's measurements do not appear to show any manifestations of the fact that there is a degeneracy in the hydrogen atom: for example, there should be two states close together in molecules which correspond to the $3p\pi$ and $3d\pi$ hydrogen states. Perhaps Scheibe's resolution was not good enough to separate them.

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