76. On the Calculation of the Electronic Reorganization of Canonical and Localized *Koopmans'* Ions

by **Martin Jungen**

Physikalisch-Chemisches Institut der Universität Basel
Klingelbergstrasse 80, CH-4056 Basel

Dem Andenken meines Doktorvaters *Heinrich Labhart* gewidmet

(16.XI.77)

Summary

Conditions and implications for the calculation of self-consistent single determinant wave functions for *Koopmans'* ions are discussed and a recipe for practical computations is given. The concept of *Koopmans'* ions has been extended to localized ions and a definition for their reorganization energies is proposed. Calculations on formaldehyde serve as a numerical illustration.

Introduction. - For many purposes it is customary to estimate ionization energies of molecules by means of *Koopmans'* theorem [1], *i.e.* to interpret the value of the orbital energies of canonical *Hartree-Fock* orbitals as ionization potentials for ionization out of the corresponding orbitals. This procedure has the advantage that we get information about the different ionization energies of a molecule from a single calculation of the ground state wave function. It is well known that the success of *Koopmans'* theorem is largely due to a cancellation of the (neglected) correlation and reorganization effects, both being of considerable magnitude but having opposite signs if the correlation energy is larger for the molecule than for the ion. More careful calculations of ionization energies have to account for these effects. This can be done by various methods, all being considerably more complicate than a *Hartree-Fock* calculation, *e.g.* with configuration mixing. Hereby the effect of mixing singly excited configurations to the *Koopmans* wave function can roughly be called reorganization whereas correlation stands for the corrections due to doubly excited configurations. However the two effects cannot strictly be distinguished. An unambiguous definition for the reorganization of a *Koopmans'* ion can be given in terms of model wave functions: The difference between a *Koopmans'* function and the best single determinant for the ionic state in question.

It is the purpose of this paper to show how the relaxation of the remaining electrons upon ionization can be treated in the framework of *Hartree-Fock* theory, *i.e.* calculating energy-optimized one-determinant wave functions for the different *Koopmans'* ions. For the ionic ground state (strictly speaking for the lowest state of each symmetry) an open-shell restricted *Hartree-Fock* calculation (*e.g.* [2] [3]) for a system with one unpaired electron is required. For higher states however the task is less trivial since orthogonality conditions to lower lying states may (and in general will) be violated if the wave function of the higher state is optimized independently (see [4-6]) and because a method of calculation using energy minimization should yield a solution corresponding to the lowest possible energy expectation value, thus the ground state wave function, if no preventing measures are taken.

To be sure since the paper by *Bagus* [7] in 1965 reorganized *Hartree-Fock* wave functions of excited *Koopmans'* ions have often been calculated for atoms and molecules. The leading determinant of the wave functions by *Meyer* and *Rosmus* (*e.g.* [8] [9]) may serve as an example; here the problems arising from non-orthogonality have successfully been neglected. For the case of inner shell hole states of atoms *Bagus* [7] has shown that the overlap between reorganized functions corresponding to ionization out of different shells is minute (the highest value quoted being 0.01). This is of course due to the spatial separation of the shells and need not apply for molecules.

Guest & Saunders [16] have shown that the total energy of a reorganized wave function corresponding to an excited *Koopmans'* ion is a variational upper bound to the exact energy value even if the orthogonality to the reorganized functions of lower *Koopmans'* ions is lost provided the energy expectation value of a lower state, calculated with the optimum orbitals of the higher ion, is not raised above the upper state. This result is a consequence of the fact that there is no direct but only second order mixing between an optimized single-determinant function and all other *Koopmans'* configurations if they are formulated with the same orbital set.

The discussion about non-orthogonality conceals the more important problem of the existence of solutions. What one is looking for are side minima of the hypersurface of energy expectation values (not local minima in a geometrical sense but minima of the energy as a function of variation parameters). Such minima may - but need not - exist. A further question is whether a minimum can unequivocally be interpreted in terms of orbitals. We believe in the existence of side minima corresponding to reorganized *Koopmans'* ions because we believe in the physical reality of the picture given by MO theory and this belief is justified as long as reorganization can be calculated since also relaxation should be a feasible physical concept. If the *Koopmans* wave function for an ionic state is not approximately equivalent to a stable self-consistent solution we are confronted with a failure of the MO picture.

In the following we shall discuss the formal conditions to be fulfilled for a successful calculation of the reorganization effect and we shall deduce a recipe for its practical realization.

Formalism. - Let us take as a starting point the closed shell *Hartree-Fock* solution for the neutral molecule, *i.e.* the self-consistent (doubly occupied and virtual) eigenfunctions φ_n of the operator $\mathscr{F}$

$$\mathscr{F} = h + \sum_{n}^{\mathrm{occ}} (2\mathscr{J}^{n} - \mathscr{K}^{n}). \tag{1}$$

Assume that an electron occupying the orbital φ_i is removed. The reorganized wave function is solution of the open shell *Hartree-Fock* problem with an operator $\mathscr{F}_i$ (see *e.g.* [3] [10])

$$\mathcal{F}_i = h + \sum_{n\neq i}^{\mathrm{occ}}{}'(2\mathcal{J}^n - \mathcal{K}^n) + \left\{\begin{array}{lll} \mathcal{J}^i - \frac{1}{2}\mathcal{K}^i & \text{(d-d, d-v)} & \text{(2a)} \\ \mathcal{J}^i - \mathcal{K}^i & \text{(s-s, s-v)} & \text{(2b)} \\ \mathcal{J}^i & \text{(d-s).} & \text{(2c)} \end{array}\right.$$

(The open shell operator consists of three differing parts, depending on the matrix elements to be constructed. (2a) connects doubly occupied orbitals with each other and doubly occupied orbitals with virtual orbitals, (2b) singly occupied orbitals and singly occupied with virtual orbitals, (2c) connects doubly and singly occupied orbitals. The matrix to be diagonalized can easily be composed from (2a–c) if the orbitals of the previous iteration are used as a basis. If the operators (2b, c) are replaced by (2a) we get the simplified 'half-electron operator' [10–12]). Let us define now an operator $\mathcal{F}_i(\lambda) = (1-\lambda)\mathcal{F} + \lambda\mathcal{F}_i$. From (1) and (2) follows

$$\mathcal{F}_i(\lambda) = \mathcal{F} - \lambda \cdot \left\{\begin{array}{lll} \mathcal{J}^i - \frac{1}{2}\mathcal{K}^i & \text{(d-d, d-v)} & \text{(3a)} \\ \mathcal{J}^i & \text{(s-s, s-v)} & \text{(3b)} \\ \mathcal{J}^i - \mathcal{K}^i & \text{(d-s)} & \text{(3c)} \end{array}\right.$$

where $0 \leqslant \lambda \leqslant 1$; $\mathcal{F}_i(0) = \mathcal{F}$, $\mathcal{F}_i(1) = \mathcal{F}_i$. We shall interpret $\mathcal{F}_i(\lambda)$ later on as an operator corresponding to ionization of λ electrons out of φ_i. Note that the matrix elements of the additional operator $\mathcal{J}^i - \mathcal{K}^i$ in (3c) between the singly occupied orbital φ_i and any doubly occupied orbital φ_d vanish since (with the usual notations)

$$\langle \varphi_i | \mathcal{J}^i - \mathcal{K}^i | \varphi_d \rangle = (\varphi_i \varphi_i | \varphi_i \varphi_d) - (\varphi_i \varphi_i | \varphi_i \varphi_d) \equiv 0 . \qquad (4)$$

No similar results can be derived for the operators (3a, b).

Theory. – A successful calculation of the reorganization of a *Koopmans'* state meets the following conditions in order to guarantee that the correct side minimum will be attained:

– During the iterative process the wave function should be modified smoothly since an abrupt change could lead out of the desired depression of the hypersurface. We achieve this by varying λ (see (3)) from 0 to 1 in the course of the first few iterations.

– The singly occupied orbital φ_i must not exchange its character with doubly occupied orbitals through mixing caused by the diagonalizations. This condition is fulfilled automatically if the orbitals are changed smoothly enough. Assume that for a given λ_o we know the self-consistent eigenfunctions of the operator $\mathcal{F}_i(\lambda_o)$ (3). For small $\delta\lambda$ the eigenfunctions of

$$\mathcal{F}_i(\lambda_o + \delta\lambda) = \mathcal{F}_i(\lambda_o) - \delta\lambda \cdot \left\{\begin{array}{lll} \mathcal{J}^i - \frac{1}{2}\mathcal{K}^i & \text{(d-d, d-v)} & \text{(5a)} \\ \mathcal{J}^i & \text{(s-s, s-v)} & \text{(5b)} \\ \mathcal{J}^i - \mathcal{K}^i & \text{(d-s)} & \text{(5c)} \end{array}\right.$$

can be calculated with perturbation theory. Because of (4) and (5c) and because $\mathcal{F}_i(\lambda_0)$ is diagonal there will be no mixing of singly and doubly occupied orbitals since the connecting matrix elements vanish. Here is the formal reason for the feasibility of such calculations. Note that this mixing would not be avoided by the half-electron operator ((5a) replacing (5b,c)). In practice the variation of λ is carried out in a number of equal steps, each one consisting of a single iteration and the critical matrix elements are zeroed artificially.

- After each iteration the singly occupied orbital must be detected again so that the desired occupation scheme can be generated for the next iteration. This is most easily achieved if the orbitals are not arranged in energetical order after diagonalization (in contrast to what is done usually in *Hartree-Fock* calculations). So the labelling of the orbitals remains unchanged throughout the whole procedure.

The above considerations indicate a way of calculating the reorganization of localized *Koopmans'* ions. A localized *Koopmans* wave function is the single determinant function originating from a localized closed shell *Hartree-Fock* determinant if one electron is removed without changing the remaining orbitals. The diagonal matrix element of the *Fock* operator (1) corresponding to the singly occupied orbital can serve for an estimation of the ionization energy in *Koopmans'* approximation. Although neither a localized ion nor its ionization energy are physical concepts in a spectroscopical sense they can be used for formal purposes in the same way as atomic orbitals and their basis energies contribute to molecular orbitals and orbital energies. It can be shown [13] that the reorganization energy of localized ions is a transferable quantity which can be used for the estimation of the reorganization, polarization and semiinternal correlation effects of canonical *Koopmans'* ions.

We calculate the reorganization of localized ions by the same method as for canonical ions, the only difference being that the matrix elements between doubly and singly occupied orbitals do not vanish automatically (because the *Fock* operator (1) is not diagonal in the basis of localized orbitals) but have to be put equal to zero artificially throughout the whole iterative process. Thus the reorganization of a localized *Koopmans'* ion has been defined in an unambiguous way.

Results. - *Calculations on Formaldehyde.* For a numerical illustration I choose the first molecule I had studied when I was a student of *Heinrich Labhart* [14]. H_2CO is well suited for a test of the reorganization behaviour since this molecule contains single and double bonds, lone pairs and a heteroatom. The calculations have been carried out using a (7s/3p)-basis of *Roos & Siegbahn* [15] augmented by d-type polarization functions (with exponent 0.6) centered on the oxygen atom. The results - numbers representing the charge distributions of the *Hartree-Fock* orbitals and of the ionic wave function in *Koopmans'* approximation and including reorganization as well as an overlap matrix of the reorganized determinants - are collected in *Tables 1-4*. More detailed information can be obtained from the author on request.

The following qualitative observations have been made:

a) *Existence of solutions.* Stable solutions have been found for all inner shell and canonical as well as localized valence *Koopmans'* ions. The reorganization energies are in the range from 0.8 eV to 20 eV.

b) *Orthogonality.* The overlap between the two inner shell states and between inner shell and valence states is negligible. The overlap integrals of different canonical valence states amount up to 0.27 after reorganization *(Table 4).* According to the test proposed by *Guest & Saunders* [16] all total energies are variational upper bounds however.

c) *Dependence of the reorganization upon the ionized orbital.* The reorganization energy of inner shell hole states is much larger than for ionization in the valence

Table 1. Hartree-Fock *orbitals of H_2CO* (formaldehyde). For these orbitals the coordinates of the charge centers and the radii of the charge distributions ($LX=(\langle X^2\rangle - \langle X\rangle^2)^{1/2}$ *etc.*) are given together with a characterization of the orbitals. Coordinates of the nuclei: C at the origin, O at X = 1.21 Å, H at X = −0.55 Å, Y = ±0.94 Å

	X (Å)	Y	Z	LX	LY	LZ	Symmetry	Characterization		
Inner shell orbitals										
1	1.210	0	0	0.070	0.070	0.070	a_1	1s(O)		
2	0	0	0	0.095	0.096	0.096	a_1	1s(C)		
Localized valence orbitals										
3	0.737	0	±0.237	0.532	0.361	0.477	a_1+b_1	'banana bonds' (BB)		
4	−0.387	±0.639	0	0.440	0.503	0.427	a_1+b_2	C−H bonds (CH)		
5	1.326	±0.278	0	0.413	0.402	0.351	a_1+b_2	lone pairs (LP)		
Canonical valence orbitals								%BB	%CH	%LP
6	0.875	0	0	0.452	0.384	0.376	a_1	70	3	27
7	−0.043	0	0	0.855	0.632	0.435	a_1	1	79	20
8	0.194	0	0	0.733	0.790	0.382	b_2		65	35
9	0.909	0	0	0.930	0.431	0.351	a_1	29	18	53
10	0.783	0	0	0.647	0.384	0.674	b_1	100		
11	0.635	0	0	0.893	0.747	0.353	b_2		35	65

Table 2. *Charge centers and radii of the charge distributions* (averaged over the occupied orbitals), *for the ionic wave functions of H_2CO in* Koopmans' *approximation without reorganization.* Note the invariance of the sum of the ionization energies upon localization in contrast to *Table 3*

	X (Å)	Y	Z	LX	LY	LZ	IP (eV)
Inner shell states							
1	0.528	0	0	0.805	0.526	0.398	560.81
2	0.609	0	0	0.808	0.526	0.398	308.95
Localized valence states							
3	0.559	0	±0.016	0.810	0.518	0.374	23.04
4	0.634	±0.043	0	0.774	0.481	0.383	19.62
5	0.520	±0.019	0	0.791	0.510	0.388	19.29
Canonical valence states							
6	0.550	0	0	0.810	0.517	0.387	38.45
7	0.611	0	0	0.776	0.500	0.383	23.63
8	0.596	0	0	0.794	0.485	0.386	18.88
9	0.548	0	0	0.782	0.514	0.388	17.30
10	0.556	0	0	0.804	0.517	0.359	13.94
11	0.566	0	0	0.790	0.489	0.388	11.68

shell. The valence orbitals are modified strongly and transformed into orbitals of the corresponding 'Z+1 molecule' (H_2CF^+ or H_2NO^+). The smallest reorganizations appear if an essentially C–H bonding canonical orbital is ionized; also in the localized case the smallest reorganizations arise from ionization out of C–H bonds. In accordance with the findings of *Guest & Saunders* [16] contracted *Hartree-Fock* orbitals seem to be accompanied with relatively large reorganization energies and spreadout orbitals with small reorganizations. The numerical results do not allow an exact confirmation of this statement but on the other hand the mean radii of the charge ellipsoids *(Table 1)* give only a crude description of the charge distribution.

d) *Canonical and localized Koopmans' ions.* In the average the reorganization energies of localized ions are larger than for canonical *Koopmans'* ions because localized orbitals are more contracted than canonical MO's. Hence the sum of the reorganization energies is not invariant upon transformation of the *Hartree-Fock* orbitals.

e) *Effect on the electronic charge distribution* (see *Tables 2 and 3*). In all cases a shifting of the charge center (as a rule towards the charge center of the ionized

Table 3. *Charge centers and radii of the charge distributions* (averaged over the occupied orbitals) *for the reorganized single determinant ionic wave functions of H_2CO.* Comparison with *Table 2* shows the effect of reorganization: Shifting and contraction of the electronic charge

	X (Å)	Y	Z	LX	LY	LZ	IP (eV)	ΔE_{reorg} (eV)
Inner shell states								
1	0.589	0	0	0.780	0.479	0.353	540.68	20.13
2	0.589	0	0	0.771	0.469	0.373	296.08	12.87
Localized valence states								
3	0.586	0	± 0.012	0.786	0.488	0.356	20.85	2.19
4	0.613	± 0.028	0	0.766	0.466	0.377	17.86	1.76
5	0.567	± 0.015	0	0.778	0.483	0.365	15.46	3.83
Canonical valence states								
6	0.585	0	0	0.788	0.485	0.366	35.78	2.67
7	0.604	0	0	0.766	0.481	0.372	22.77	0.86
8	0.598	0	0	0.780	0.465	0.375	18.05	0.83
9	0.571	0	0	0.768	0.488	0.367	14.64	2.66
10	0.583	0	0	0.786	0.490	0.342	12.16	1.78
11	0.582	0	0	0.780	0.472	0.368	9.37	2.31

Table 4. *Overlap matrix for the reorganized wave functions of the canonical* Koopmans' *ions* of H_2CO (in exponential notation). The numbering of the states corresponds to the numbers of *Table 3*

1 (A_1)	2 (A_1)	6 (A_1)	7 (A_1)	8 (B_2)	9 (A_1)	10 (B_1)	11 (B_2)	
1	0.286−4	0.352−2	0.160−2	0	0.132−2	0	0	1 (A_1)
	1	0.399−2	−0.472−2	0	−0.176−2	0	0	2 (A_1)
		1	−0.115+0	0	0.353−1	0	0	6 (A_1)
			1	0	0.268+0	0	0	7 (A_1)
				1	0	0	−0.260+0	8 (B_2)
					1	0	0	9 (A_1)
						1	0	10 (B_1)
							1	11 (B_2)

orbital) and a contraction of the charge distribution by some percents of an Å are observed. The effect on individual orbitals is much larger than the perturbation of the total charge density because orbitals are subject not only to the perturbing potential but also to mutual orthogonality conditions. As a rule the net shifting of the charge center results from mutually opposite orbital shiftings which can be larger by an order of magnitude.

f) *Effect on the singly occupied orbital.* In the majority of cases the shape of the singly occupied orbital is not drastically modified; this does not apply to the highest three canonical orbitals (in these cases the calculation was significantly more difficult to be carried out although the corresponding ionic functions are the lowest ones of their symmetry). The singly occupied orbital has always been contracted; no 'spreading-out of the surplus positive charge' could be observed.

Conclusions. - We have shown that the electronic relaxation of canonical *Koopmans'* ions can successfully be calculated due to the fact that there is no direct mixing of singly and doubly occupied orbitals. Thus the orbital characterizations are maintained under the relaxation process to a good approximation and therefore the reorganized wave functions can be identified with *Koopmans'* functions. If similar conditions are imposed artificially the relaxation of localized *Koopmans'* ions can be defined and calculated.

The results on formaldehyde indicate that the effect of relaxation can be characterized as coulombic interaction between a positive charge in the emptied orbital and the remaining electrons. The more the positive charge is pointlike the larger will be its influence. This is particularly true for localized orbitals because of the small contribution of exchange corrections. As a rule the change of the emptied orbital itself is less drastic than the change of the charge density of the doubly occupied orbital space. On the other hand we find often a strong mixing of the doubly occupied orbitals among themselves.

This work is part of the project Nr. 2.733-0.77 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.*

REFERENCES

[1] *T. Koopmans,* Physica *1,* 104 (1934).
[2] *C.C.J. Roothaan,* Revs. mod. Physics *32,* 179 (1960).
[3] *R. McWeeny,* 'Molecular Orbitals in Chemistry, Physics and Biology', p. 305, New York, Academic Press 1964.
[4] *C.S. Sharma & C.A. Coulson,* Proc. phys. Soc. *80,* 81 (1962).
[5] *M. Cohen & A. Dalgarno,* Revs. mod. Physics *35,* 506 (1963).
[6] *D. Layzer,* Phys. Rev. *132,* 735 (1963).
[7] *P.S. Bagus,* Phys. Rev. *139,* A619 (1965).
[8] *W. Meyer,* J. chem. Physics *58,* 1017 (1973).
[9] *P. Rosmus, P.D. Dacre, B. Solouki & H. Bock,* Theor. chim. Acta *35,* 129 (1974).
[10] *H.C. Longuet-Higgins & J.A. Pople,* Proc. phys. Soc. *A 58,* 591 (1955).
[11] *M.J.S. Dewar, J.A. Hashmall & C.G. Venier,* J. Amer. chem. Soc. *90,* 1953 (1968).
[12] *M. Jungen,* Theor. chim. Acta *11,* 193 (1968).
[13] *W. Müller & M. Jungen,* to be published.
[14] *M. Jungen, H. Labhart & G. Wagnière,* Theor. chim. Acta *4,* 305 (1966).
[15] *B. Roos & P. Siegbahn,* Theor. chim. Acta *17,* 209 (1970).
[16] *M.F. Guest & V.R. Saunders,* Mol. Physics *29,* 873 (1975).