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PERTURBATION EXPANSION FOR BOND ORDERS AND THE COMMUTATOR [H, S] *

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SUMMARY: A perturbative expansion for Chirgwin and Coulson's and Lowdin's definitions of bond order is obtained, introducing explicity the commutator [H, S]. Projection operator formalism is used in the development of the perturbation theory. Recurrence formulae are obtained for the corrections up to any order. The relation between both definitions is given.

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INTRODUCTION

In a previous paper [1], we have calculated charges and bond orders for pyridine following the LCAO-MO method, taking into account all the overlap integrals, and using Chirgwin and Coulson's formulae [2]. These results are appreciably different from these obtained neglecting overlap (see table). It is well known [2] that, if H and S (H, hamiltonian matrix; S, overlap matrix) commute, both calculations must yield the same results. In our case H and S did not commute; we therefore attempted to analyse qualitatively the commutator's role in these circumstances. We calculated the commutator's eigenvalues, and saw how many common principal directions H and S had.

Löwdin [3] has proposed alternative definitions for charges (q) and bond orders (p) including overlap. When H and S commute, these formulae reduce also to the well-known definitions of charges and bond orders used on neglecting overlap. In the table, we show q and p for pyridine, as obtained from Löwdin's treatment.

Both treatments suggest further developments for the case when H and S do not commute. This seems worth doing psecially because, unlike to what is said in reference [2], charges and bond orders calculated with and without overlap, may be quite different even in simple cases, as we mentioned above for the pyridine.

Therefore, we shall apply perturbation theory to Chirgwin and Coulson's bond order formulae, and also to Löwdin's, taking for the perturbation the non-diagonal part of S. To see more closely the relation between bond order and the commutator [H,S], we shall introduce it explicitly in the expansion.

For this perturbation theory, we shall use-with the Chirgwin and Coulson's definitions - the projection operator, following a formalism somewhat different from that utilized by Löwdin [4]. In this way, simple formulae may be obtained, which permits calculate the correction to the bond order up to any desired order.

PERTURBATION EXPANSION WITH CHIRGWIN AND COULSON'S FORMULAE

Bond orders are defined by these authors as:

$$p_c = \frac{1}{2} \sum_i n_i (S|x_i\rangle\langle x_i| + |x_i\rangle\langle x_i|S) \quad (1)$$

where $|x_i\rangle$ is determined by:

$$(H - \lambda_i S)\, |x_i\rangle = 0 \quad (2)$$

with the condition

$$\langle x_i|S|x_j\rangle = \delta_{ij} \quad (3)$$

We shall develop a perturbation expansion for p in power of S' by writing:

$$S = 1 + S' \quad (4)$$

as done by Lowdin [3]. Let us define the auxiliary operators

$$p_i = S|x_i\rangle\langle x_i| \quad (5)$$

The orthogonality condition (3) is equivalent to:

$$p_i p_j = \sigma_{ij}\, p_j \qquad (6)$$

that is, p_i is idempotent

$$\boxed{p_i^2 = p_i} \qquad (7)$$

Let us now transform equation (2) so as to become an equation for p_i. We have $\lambda_i = \langle x_i|H|x_i\rangle$. Then, multiplying (2) on the right by $\langle x_i|S$ one obtains:

$$Hp_i^T - p_i Hp_i^T = 0$$

and taking the transpose:

$$p_i H - p_i Hp_i^T = 0$$

A comparison of these two equations give:

$$\boxed{p_i H = Hp_i^T} \qquad (8)$$

Let us now write:

$$p_i = p_i^o + p_i' \qquad (9)$$

where $p_i^o = |x_i^o\rangle\langle x_i^o|$, the projection operator into the eigenstate $|x_i^o\rangle$ of H, satisfies the equation:

$$Hp_i^o = \lambda_i^o p_i^o \qquad (10)$$

and the orthogonality relation

$$p_i^o p_j^o = \sigma_{ij} p_j^o \qquad (11)$$

Then (8) becomes:

$$p_i' H = Hp_i'^T$$

which shows that we can write:

$$p_i' = H\, \Pi_i \qquad (12)$$

where $\Pi_i^T = \Pi_i$. Then equation (9) becomes:

$$|x_i\rangle\langle x_i| = S^{-1}(p_i^o + H\Pi_i)$$

and since the left hand side is symmetric we obtain:

$$S^{-1}(p_i^o + H\Pi_i) = (p_i^o + \Pi_i H)S^{-1}$$

which upon multiplication on both sides by S gives:

$$p_i^o S + H\Pi_i S = S p_i^o + S\Pi_i H$$

and

$$H\Pi_i S - S\Pi_i H = S p_i^o - p_i^o S \tag{13}$$

which is the fundamental equation for Π_i. In addition Π_i must satisfy condition (7):

$$(p_i^o + H\Pi_i)^2 = p_i^o + H\Pi_i$$

which gives:

$$\boxed{H\Pi_i H\Pi_i = H\Pi_i - p_i^o H\Pi_i - H\Pi_i p_i^o} \tag{14}$$

Now we make a perturbation expansion for Π_i, that is $\Pi_i = \sum_{n=1}^{\infty} \Pi_i^n$. Then (13) and (14) give:

$$H\Pi_i^1 - \Pi_i^1 H = S' p_i^o - p_i^o S' \tag{15}$$

$$H\Pi_i^{n+1} - \Pi_i^{n+1} H = S'\Pi_i^n H - H\Pi_i^n S' \tag{16}$$

$$H\Pi_i^1 - p_i^o H\Pi_i^1 - H\Pi_i^1 p_i^o = 0 \tag{17}$$

$$H\Pi_i^{n+1} - p_i^o H\Pi_i^{n+1} - H\Pi_i^{n+1} p_i^o = \sum_{q=1}^{n} H\Pi^q H\Pi^{n+1-q} \tag{18}$$

Equation (16) is a simple recurrence formula which, as we shall see, allows us to determine the correction to the bond order up to any desired order, once the first order correction is known.

The orthonormality relations (11) are equivalent to:

$$\sum_j p_j^o = 1 \tag{19}$$

Then we can write:

$$\Pi_i^n = \sum_{j,k} p_j^o \, \Pi_i^n \, p_k^o \tag{20}$$

Equations (15) to (18) give, on multiplying by p_j^o on the left, and by p_i^o or p_k^o on the right:

$$(j \neq i) \qquad p_j^o \, \Pi_i^1 \, p_i^o = \frac{p_j^o \, S' p_i^o}{\lambda_j^o - \lambda_i^o} \tag{21}$$

$$(1 - \delta_{ij} - \delta_{ik}) \, p_j^o \, \Pi_i^1 \, p_k^o = 0 \tag{22}$$

$$(j \neq k) \quad p_j^o \, \Pi_i^{n+1} \, p_k^o = \frac{1}{\lambda_j^o - \lambda_k^o} \sum_\ell \Big\{ (p_j^o \, S' p_\ell^o)(p_\ell^o \Pi_i^n p_k^o)\lambda_k^o -$$

$$- (p_j^o \Pi_i^n p_\ell^o)(p_\ell^o S' p_k^o)\lambda_j^o \Big\} \tag{23}$$

$$(1 - \delta_{ij} - \delta_{ik}) p_j^o \, \Pi_i^{n+1} \, p_k^o = \sum_{q=1}^{n} \sum_\ell (p_j^o \, \Pi_i^n \, p_\ell^o)(p_\ell^o \Pi_i^{n+1-q} p_k^o)\lambda_\ell^o \tag{24}$$

Knowing the first order correction to p, formulae (23) and (24) lead to the higher order corrections.

With equations (21) and (22), and remembering (20), the first order correction is easily obtained:

$$\Delta_1 p = \sum_{j \neq i} n_i \frac{\lambda_j^o + \lambda_i^o}{\lambda_j^o - \lambda_i^o} \, p_j^o \, S' \, p_i^o \tag{25}$$

Let us calculate the expressions (23) and (24) for the second order correction:

$$(j \neq k)(j,k \neq i)\, p_j^o \Pi_i^2 p_k^o = \lambda_i^o \frac{(p_j^o S' p_i^o)(p_i^o S' p_k^o)}{(\lambda_j^o - \lambda_i^o)(\lambda_k^o - \lambda_i^o)} \tag{26}$$

$$(j \neq i) \quad p_j^o \Pi_i^2 p_i^o = \frac{1}{\lambda_j^o - \lambda_i^o} \left\{ \sum_\ell \frac{\lambda_i^o}{\lambda_\ell^o - \lambda_i^o} (p_j^o S' p_\ell^o)(p_\ell^o S' p_i^o) - \right.$$

$$\left. - \frac{\lambda_j^o}{\lambda_j^o - \lambda_i^o} (p_j^o S' p_i^o)(p_i^o S' p_i^o) \right\} \tag{27}$$

$$p_i^o \Pi_i^2 p_i^o = - \sum_\ell \frac{\lambda_\ell^o}{(\lambda_\ell^o - \lambda_i^o)^2} (p_i^o S' p_\ell^o)(p_\ell^o S' p_i^o). \tag{28}$$

For the corresponding bond order correction:

$$\Delta_2 p = \frac{1}{2} \sum_{j,k \neq i} n_i \frac{\lambda_i^o}{(\lambda_j^o - \lambda_i^o)(\lambda_k^o - \lambda_i^o)} \left[(\lambda_j^o + \lambda_k^o)\, \phi_{jik} + (\lambda_j^o + \lambda_i^o)(\phi_{jki} + \phi_{ikj}) \right] -$$

$$- \frac{1}{2} \sum_{j \neq i} n_i \frac{\lambda_j^o}{(\lambda_j^o - \lambda_i^o)^2} \left[2\lambda_i^o \phi_{iji} + (\lambda_j^o + \lambda_i^o)(\phi_{jii} + \phi_{iij}) \right], \tag{29}$$

where

$$\phi_{jik} = (p_j^o S' p_i^o)(p_i^o S' p_k^o) = \langle x_j^o | S' | x_i^o \rangle \langle x_i^o | S' | x_k^o \rangle \, | x_j^o \rangle \langle x_k^o | \tag{30}$$

The operator $p_j^o S' p_k^o$ whit $j \neq k$ may be related to the commutator $[H, S']$ by

$$p_j^o S' p_k^o = \frac{p_j^o [H, S'] p_k^o}{\lambda_j^o - \lambda_k^o} \tag{31}$$

Since the first order correction to p_i depende only on operators of this form, then from the recurrence relations (23) and (24) it follows that the corrections to all orders contain the commutator (through the operator (31) as a factor. However one can verify that higher order correction also depend on S' through terms $p_j^o S' p_j^o$.

PERTURBATION EXPANSION WITH LOWDIN'S FORMULAE

Here the hamiltonian H is replaced by

$$H' = (1+S')^{-\frac{1}{2}} H (1+S')^{-\frac{1}{2}} \simeq H - \frac{1}{2}(S'H + HS') + \frac{1}{4} S'HS' + \frac{3}{8}(S'^2H + HS'^2) =$$

$$= H + V' + V'' \qquad (32)$$

to second order. The term $(V' + V'')$ represents the perturbation, as suggested by Löwdin [3].

With classical perturbation theory, we have in first order:

$$|x_i^1\rangle = \sum_k c_{ik}^{(1)} |x_k^o\rangle ; \quad c_{ii}^{(1)} = 0 ; \quad c_{ik}^{(1)} = c_{ki}^{(1)} ;$$
$$c_{ik}^{(1)} = \frac{\langle x_k^o | V' | x_i^o \rangle}{\lambda_i^o - \lambda_k^o} , \quad \lambda_i^{(1)} = \langle x_i^o | V' | x_i^o \rangle \qquad (33)$$

The bond order operator p is now defined by:

$$p_i = \sum_i n_i |x_i\rangle \langle x_i| \simeq p^o + \Delta_1 p + \Delta_2 p$$

where $|x_i\rangle$ satisfies the secular equation $(H' - \lambda_i)|x_i\rangle = 0$. We have then, in first order

$$\Delta_1 p = \sum_i n_i \left\{ |x_i^1\rangle \langle x_i^o| + |x_i^o\rangle \langle x_i^1| \right\} =$$

$$= \sum_{i,k} n_i c_{ik}^{(1)} \left\{ |x_k^o\rangle \langle x_i^o| + |x_i^o\rangle \langle x_k^o| \right\} \quad (34)$$

with:

$$c_{ik}^{(1)} = \frac{1}{2} \frac{\langle x_k^o | S'H + HS' | x_i^o \rangle}{\lambda_k^o - \lambda_i^o} = \frac{1}{2} \frac{\lambda_i^o + \lambda_k^o}{\lambda_k^o - \lambda_i^o} \sigma_{ik}$$

$$\sigma_{ik} = \langle x_k^o | S' | x_i^o \rangle \quad (35)$$

That is, as has been pointed by Davies [5], in first order both definition of p are equivalent, for formulae (34), (35) are identical with formula (25).

Let us see what happens in second order

$$(H - \lambda_i^o)|x_i^2\rangle + V'|x_i^1\rangle + V''|x_i^o\rangle - \lambda_i^{(1)}|x_i^1 - \lambda_i^{(2)}|x_i^o\rangle = 0$$

From normalization

$$x_i|x_i\rangle = 1; \quad c_{ii}^{(2)} = -\frac{1}{2} \sum_k c_{ik}^{(1)2}$$

Multiplying by $\langle x_k^o|$, and taking $|x_i^2\rangle = \sum_k c_{ik}^{(2)} |x_k^o\rangle$,

$$c_{ik}^{(2)} = \frac{x_k^o|V'|x_i^1\rangle + \langle x_k^o|V''|x_i^o\rangle - \lambda_i^{(1)} c_{ik}^{(1)}}{\lambda_i^o - \lambda_k^o} \quad (36)$$

$$c_{ik}^{(2)} = \frac{\frac{1}{8}\sum_j \sigma_{ij}\sigma_{jk}\left[\frac{\lambda_i^o(3\lambda_i^o+5\lambda_j^o)+\lambda_k^o(\lambda_i^o-\lambda_j^o)}{\lambda_i^o-\lambda_j^o}\right] - \left[\frac{6\lambda_i^o\lambda_k^o+3\lambda_k^{o2}-\lambda_i^{o2}}{8(\lambda_i^o-\lambda_k^o)}\right]\langle x_i^o|S|x_i^o\rangle\sigma_{ik}}{\lambda_i^o - \lambda_k^o}$$

Hence

$$\Delta_2 p = \sum_i n_i \left\{ |x_i^2\rangle\langle x_i^o| + |x_i^o\rangle\langle x_i^2| + |x_i^1\rangle\langle x_i^1| \right\}$$

that is,

$$\Delta_2 p = \sum_i n_i \left\{ \sum_k c_{ik}^{(2)} \left[|x_k^o \quad x_i^o| + |x_i^o \quad x_k^o| \right] + \sum_{k,\ell} c_{ik}^{(1)} c_{i\ell}^{(1)} |x_k^o\rangle\langle x^o \right\} \qquad (37)$$

Let us note that the matrix elements of the commutator which appear in these expansions, are different from the eigen values which we calculated in reference [1], for the present matrix elements refer to the representation where H is diagonal, which is in general distinct from that for which [H,S] is diagonal.

RELATION BETWEEN CHIRGWIN AND COULSON'S AND LOWDIN'S DEFINITIONS BOND ORDERS

The above definitions of bond order are related as follows:

$$p_c = \frac{1}{2}\left[S^{\frac{1}{2}} p_L S^{-\frac{1}{2}} + S^{-\frac{1}{2}} p_L S^{\frac{1}{2}} \right]$$

To second order:

$$p_c = p_L + \sum_i n_i \left[-\frac{1}{4} S' p_i^o S' + \frac{1}{8} (p_i^o S'^2 + S'^2 p_i^o) \right]$$

As we already saw, p_c and p_L coincide up to first order.

The second order terms of p_L can also be determined from (29) and (39). The result is:

$$\Delta_2 p = \frac{1}{2} \sum_{(j,k)\neq i} n_i \frac{1}{(\lambda_j^o - \lambda_i^o)(\lambda_k^o - \lambda_i^o)} \left\{ \frac{1}{2} (\lambda_j^o + \lambda_i^o)(\lambda_k^o + \lambda_i^o)\phi_{jik} + \right.$$

$$\left. + \left[(\lambda_j^o + \lambda_i^o)\lambda_i^o - \frac{1}{4} (\lambda_j^o - \lambda_i^o)(\lambda_k^o - \lambda_i^o) \right] (\phi_{jki} + \phi_{ikj}) \right\} -$$

$$- \frac{1}{2} \sum_{j \neq i} n_i \frac{1}{(\lambda_j^o - \lambda_i^o)^2} \left\{ \frac{(\lambda_j^o + \lambda_i^o)^2}{2} \phi_{iji} + \left[\frac{(\lambda_j^o - \lambda_i^o)}{2} + 2\lambda_i^o \lambda_j^o \right] (\phi_{jii} + \right.$$

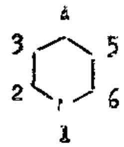
$$\left. + \phi_{iij}) \right\} \qquad 40)$$

which may be verified to be equivalent to (37).

Straighforward numerical calculation of q and p-starting from their original expressions the results of which are shown in the table, throws light on these formulae. It is seen that the value of q and p obtained according to Chirgwin and Coulson's or Lowdin's method, are much closer them than they are to those obtained supposing $S = 0$. This is of course expected, for both definitions differ between them only in second order, while they differ in first order from the difinitions without overlap. With $S = 0$, for instance, the results for p under iii) would predict that the distance 3-4 is smaller than the distance 2-3, in disagreement with i) and ii).

From the point of view of the results, both treatments seem to be equivalent, even when overlap is far from negligible. Chirgwin and Coulson's is perhaps somewhat easier for calculation. On the other hand, to Lowdin's bond order it could be assigned a physical meaning, that is the matrix electron density; its diagonal elements (charges) would represent the probability of finding an electron in one of the orthonormal states.

TABLE: Charges (q), bond orders (p), and free valance numbers (f), for pyridine, calculated following Chirgwin and Coulson (i), Lowdin (ii) and without overlap (iii) *.

	(i)	(ii)	(iii)
q_1	1.203	1.153	1.435
q_2	0.936	0.960	0.947
q_3	0.969	0.973	0.882
q_4	0.986	0.981	0.907
p_{12}	0.640	0.643	0.609
p_{23}	0.701	0.693	0.638
p_{34}	0.649	0.652	0.671
f_1	0.500	0.500	0.525
f_2	0.461	0.444	0.699
f_3	0.314	0.340	-0.005
f_4	0.446	0.427	0.105

* The matrices H and S which we have used for the calculation are taken from reference (1).

S is obtained using Kohlrausch's nuclear effective charges.

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