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Evaluation of Molecular Magnetic Properties and Some Related Approximations

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Small magnetic terms in the molecular Hamiltonian are treated in a SCF perturbation scheme, using H.F. molecular orbitals as basis; some approximations are discussed and compared. In particular, the paramagnetic contributions to the susceptibility and nuclear shielding constants for LiH and N_2 are investigated and discussed.

Es werden verschiedene Näherungen für Störungsrechnungen, kleine magnetische Terme eines molekularen Hamiltonoperatores betreffend, im H. F.-Schema diskutiert, speziell die Rechnungen für LiH- und N_2-Moleküle, die sich auf den paramagnetischen Teil der Suszeptibilität und die Abschirmungskonstante für verschiedene Kerne beziehen.

Des approximations différentes qu'on peut choisir dans les calculs perturbatifs des éléments petits d'une Hamiltonienne moléculaire, sur une basis de Hartree-Fock, viennent examinées et comparées. En particulier, on présent les calculs rélatifs á la partie paramagnétique de la susceptibilité et de la constante d'écran nucléaire des molècules LiH et N_2.

I. Introduction

The evaluation of molecular observables, associated with magnetic interactions, has been the subject of many papers appeared in rather recent years. Different methods, proposed by various authors, have sometimes enabled one to obtain results which fairly fit experimental data [*2—6, 10—14*].

Due to the smallness of the Hamiltonian terms corresponding to magnetic interactions, it seems very natural to approach the problem from a perturbative point of view. Our knowledge of molecular wave functions, however, is far from being complete. As a matter of fact, in most cases, we have a wave function for ground states, approximated by a Slater determinant, built up with SCF MO LCAO orbitals, and essentially for small molecules. Perturbation theory in the SCF scheme is well known, and has been reconsidered, by several authors, in versions often only formally different [*1, 7, 10, 15*]. In this paper we shall investigate some approximations of the above theory, and compare the results on the basis of two simple examples (LiH and N_2 molecules).

II. Theory

Let us assume that we have solved the unperturbed H.F. molecular problem, so that we dispose with a set of orthonormal one-electron orbitals, $\Phi_j^{(0)}$ ($j = 1, 2, \ldots, M$), the eigenstates of the H.F. Hamiltonian operator $f^{(0)}$:

$$f^{(0)} \Phi_j^{(0)} = \varepsilon_j^{(0)} \Phi_j^{(0)} .$$

Such a set of orthonormal functions will be exploited as basis for a perturbation treatment of molecular problems.

In the presence of perturbing fields, the molecular Hamiltonian can be written as

$$\mathscr{H} = \mathscr{H}_t^{(0)} + \mathscr{H}_p , \quad (1)$$

where $\mathscr{H}_t^{(0)}$ is now the true Hamiltonian for the unperturbed molecular system, and $\mathscr{H}_p$ is the operator corresponding to a generic one-electron perturbation, developable in terms of perturbation orders, so that we can write:

$$\mathscr{H}_p = \mathscr{H}^{(\mathrm{I})} + \mathscr{H}^{(\mathrm{II})} + \dots . \tag{2}$$

For the observables which this paper is interested in, we have:

$$\mathscr{H}_p = \mathscr{H}^{(\mathrm{I})} + \mathscr{H}^{(\mathrm{II})} ,$$

$$\mathscr{H}^{(\mathrm{I})} = \sum_{j=1}^{2N} \boldsymbol{h}^{(1)}(j) , \qquad \mathscr{H}^{(\mathrm{II})} = \sum_{j=1}^{2N} \boldsymbol{h}^{(2)}(j) ,$$

$$\boldsymbol{h}^{(1)} = \tfrac{1}{2}\alpha\left(\vec{H}\cdot\vec{\mathscr{L}} + 2\,\frac{\vec{\mu}\cdot\vec{\mathscr{L}}}{r^3}\right),$$

$$\boldsymbol{h}^{(2)} = \tfrac{1}{2}\alpha^2\left[\tfrac{1}{4}\vec{H}\cdot(r^2\boldsymbol{I} - \vec{r}\,\vec{r})\cdot\vec{H} + \vec{\mu}\cdot\left(\frac{1}{r}\boldsymbol{I} - \frac{\vec{r}\,\vec{r}}{r^3}\right)\cdot\vec{H}\right].$$

Here $\vec{H}$ is the external magnetic field, $\vec{\mu}$ the magnetic dipole moment of the nucleus whose nuclear magnetic shielding constant is to be calculated, $\vec{\mathscr{L}}$ the orbital angular momentum operator, $\boldsymbol{I}$ the unit dyadic and $\alpha = 1/137$. The gauge was chosen in such a manner that the external vector potential is zero at the nucleus which has the intrinsic magnetic moment $\vec{\mu}$.

In order to evaluate the magnetic observables we are interested in, we only need to single out the second order terms from the following expectation value of the total energy:

$$W = \frac{\langle \Psi' \mid \mathscr{H} \mid \Psi' \rangle}{\langle \Psi' \mid \Psi' \rangle} . \tag{3}$$

As far as Ψ' is concerned, we shall assume that a single determinant wave function is still a reliable approximation to the ground state of the molecule in the presence of a perturbation, i.e. we put:

$$\Psi' = (2N!)^{-\frac{1}{2}} \,\|\, \Phi_1(1)\,\alpha(1) \dots \Phi_N(2N)\,\beta(2N) \,\| , \tag{4}$$

where

$$\Phi_j = \Phi_j^{(0)} + \delta\Phi_j ,$$

$\delta\Phi_j$ being the modification induced on the unperturbed molecular orbital $\Phi_j^{(0)}$ by the perturbation. The variations $\delta\Phi_j$ may be now expanded in terms of the unperturbed $\{\Phi_k^{(0)}\}$ set, as follows:

$$\delta\Phi_j = \delta^1\Phi_j + \delta^2\Phi_j = \sum_{l=N+1}^{M} (c_{lj}^{(1)} + c_{lj}^{(2)})\,\Phi_l^{(0)} . \tag{5}$$

(The upper indices indicate the order of perturbation.) The single determinant (4) is equivalent to the following expansion in terms of Slater determinants:

$$\begin{aligned}\Psi' = \Psi^{(0)} &+ \sum_{j=1}^{N}\sum_{l=N+1}^{M} (c_{lj}^{(1)} + c_{lj}^{(2)})\mathscr{A}\left\{(1\alpha)\dots(N\beta)\frac{(l)}{(j)}\right\} + \\ &+ \sum_{j=1}^{N}\sum_{k>j}^{N}\sum_{l=N+1}^{M}\sum_{m\neq l}^{M} c_{lj}^{(1)}c_{mk}^{(1)}\mathscr{A}\left\{(1\alpha)\dots(N\beta)\frac{(l)}{(j)}\frac{(m)}{(k)}\right\} + \dots\end{aligned} \tag{6}$$

The notation used should be self-evident. It may be noted, however, that the expansion (6) is simply another way of writing the determinant (4), so that it should not be confused with a configuration interaction expansion.

By substituting Eq. (6) into the second order terms from Eq. (3), we get the following expression for $W^{(2)}$, explicitly in terms of $c_{lj}^{(1)}$ only:

$$W^{(2)} = 2\sum_{j=1}^{N}\langle \Phi_j^{(0)} \mid \boldsymbol{h}^{(2)} \mid \Phi_j^{(0)}\rangle - 2\sum_{j=1}^{N}\sum_{l=N+1}^{M}(\varepsilon_l^{(0)} - \varepsilon_j^{(0)})\, c_{lj}^{(1)}\, c_{lj}^{(1)} + $$
$$+ 4\sum_{j=1}^{N}\sum_{l=N+1}^{M} c_{lj}^{(1)} \langle \Phi_j^{(0)} \mid \boldsymbol{h}^{(1)} \mid \Phi_l^{(0)}\rangle +$$
$$+ 2\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=N+1}^{M}\sum_{m=N+1}^{M} c_{lj}^{(1)} c_{mk}^{(1)} [(\Phi_j^{(0)}\Phi_k^{(0)} \mid \Phi_l^{(0)}\Phi_m^{(0)}) - (\Phi_j^{(0)}\Phi_m^{(0)} \mid \Phi_k^{(0)}\Phi_l^{(0)})], \qquad (7)$$

where

$$(\Phi_a^{(0)}\Phi_b^{(0)} \mid \Phi_c^{(0)}\Phi_d^{(0)}) \equiv \iint \Phi_a^{(0)}(1)\,\Phi_b^{(0)}(1)\,\frac{1}{r_{12}}\,\Phi_c^{(0)}(2)\,\Phi_d^{(0)}(2)\,d\tau_1\,d\tau_2 \,.$$

[Eq. (7) has been written down for the case where the perturbation Hamiltonian $\mathscr{H}^{(1)}$ is a purely imaginary operator.]

In a rigorous perturbation SCF treatment, the coefficients are, of course, affected by the changes induced in the H.F. electronic potential by the 'external' perturbing fields. Some approximations are, however, noteworthy, and this paper is particularly concerned with these latter.

First order perturbation theory formally gives for the $c_{lj}^{(1)}$*:

$$c_{lj}^{(1)} = \frac{\langle \Phi_l^{(0)} \mid \boldsymbol{f}^{(1)} \mid \Phi_j^{(0)}\rangle}{\varepsilon_j^{(0)} - \varepsilon_l^{(0)}} \qquad (8)$$

where

$$\boldsymbol{f}^{(1)} = \boldsymbol{h}^{(1)} + \boldsymbol{g}^{(1)}\,, \qquad (9)$$

$$\boldsymbol{g}^{(1)} \mid \Phi_j^{(0)}\rangle = \sum_{k=1}^{N}\sum_{m=N+1}^{M} c_{mk}^{(1)} \left[\int \Phi_m^{(0)}(2)\,\Phi_j^{(0)}(2)\,\frac{1}{r_{12}}\,d\tau_2\,\Phi_k^{(0)}(1) - \right.$$
$$\left. - \int \Phi_k^{(0)}(2)\,\Phi_j^{(0)}(2)\,\frac{1}{r_{12}}\,d\tau_2\,\Phi_m^{(0)}(1)\right]. \qquad (10)$$

Obviously Eq. (8) is not an explicit definition of $c_{lj}^{(1)}$, since the $\boldsymbol{g}^{(1)}$ operator depends on all coefficients $c_{mk}^{(1)}$, but is, nevertheless, a useful working formula. If Eq. (8) is satisfield, Eq. (7) transforms simply into

$$W^{(2)} = 2\sum_{j=1}^{N}\langle \Phi_j^{(0)} \mid \boldsymbol{h}^{(2)} \mid \Phi_j^{(0)}\rangle + 2\sum_{j=1}^{N}\sum_{l=N+1}^{M} c_{lj}^{(1)}\langle \Phi_j^{(0)} \mid \boldsymbol{h}^{(1)} \mid \Phi_l^{(0)}\rangle\,; \qquad (11)$$

that is a well known result in perturbation theory given by many authors (e.g. see ref. [*10*]).

STEVENS et al. [*10*] propose and discuss two approximate versions of the 'exact' calculation, wich we would like to reexamine and compare with other ones also possible.

A first version investigated in [*10*] completly neglects the changes induced in the H.F. potential by the perturbation; Eq. (8) then leads to

$$c_{lj}^{(1)} = \frac{\langle \Phi_l^{(0)} \mid \boldsymbol{h}^{(1)} \mid \Phi_j^{(0)}\rangle}{\varepsilon_j^{(0)} - \varepsilon_l^{(0)}}\,, \qquad (12)$$

and these are substituted into Eq. (11).

Actually Eq. (11) has been obtained in the assumption that the $c_{lj}^{(1)}$'s satisfy Eq. (8). A different way to verify the relative importance of the changes induced in the H.F. potential is to substitute the $c_{lj}^{(1)}$'s, given by Eq. (12), into Eq. (7).

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* As an alternative way to deduce Eq. (8), one can make $W^{(2)}$ stationary with respect to variations of the $c_{lj}^{(1)}$.

This leads to the following expressions for the isotropic part of the magnetic susceptibility and nuclear magnetic shielding tensors (paramagnetic contribution only):

$$\chi^{(\mathrm{par})} = -\chi_0 \sum_{j=1}^{N} \sum_{l=N+1}^{M} \frac{\langle \Phi_j^{(0)} \mid \mathscr{L}_x \mid \Phi_l^{(0)} \rangle}{\varepsilon_j^{(0)} - \varepsilon_l^{(0)}} \Big\{ \langle \Phi_l^{(0)} \mid \mathscr{L}_x \mid \Phi_j^{(0)} \rangle - \\ - \sum_{k=1}^{N} \sum_{m=N+1}^{M} \frac{\langle \Phi_m^{(0)} \mid \mathscr{L}_x \mid \Phi_k^{(0)} \rangle}{\varepsilon_k^{(0)} - \varepsilon_m^{(0)}} \left[(\Phi_j^{(0)} \Phi_k^{(0)} \mid \Phi_l^{(0)} \Phi_m^{(0)}) - (\Phi_j^{(0)} \Phi_m^{(0)} \mid \Phi_k^{(0)} \Phi_l^{(0)}) \right] \Big\} , \tag{13}$$

$$\sigma^{(\mathrm{par})} = \sigma_0 \sum_{j=1}^{N} \sum_{l=N+1}^{M} \frac{\langle \Phi_j^{(0)} \mid \mathscr{L}_x \mid \Phi_l^{(0)} \rangle}{\varepsilon_j^{(0)} - \varepsilon_l^{(0)}} \Big\{ \langle \Phi_l^{(0)} \mid \frac{\mathscr{L}_x}{\mathrm{r}^3} \mid \Phi_j^{(0)} \rangle - \\ - \sum_{k=1}^{N} \sum_{m=N+1}^{M} \frac{\langle \Phi_m^{(0)} \left| \frac{\mathscr{L}_x}{r^3} \right| \Phi_k^{(0)} \rangle}{\varepsilon_k^{(0)} - \varepsilon_m^{(0)}} \left[(\Phi_j^{(0)} \Phi_k^{(0)} \mid \Phi_l^{(0)} \Phi_m^{(0)}) - (\Phi_j^{(0)} \Phi_m^{(0)} \mid \Phi_k^{(0)} \Phi_l^{(0)}) \right] \Big\} , \tag{14}$$

where $\chi_0 = \frac{2}{3} \mathscr{N} \alpha^2 a_0^3$, $\mathscr{N}$ being Avogadro's number, and $\sigma_0 = \frac{4}{3} \alpha^2$. The external magnetic field $\vec{H}$ lies along the x-axis, perpendicular to the molecular bond axis (z).

III. Results and Discussion

The results collected in column II of the table, have been obtained by means of Eq. (13), (14), and are to be compared with those of columns I and V. Column I shows the results obtained by substituting the approximate value for $c_{lj}^{(1)}$, Eq. (12), into Eq. (11) according to Ref. [*10*], while in column V the results of the 'exact' calculation are reported. Our approximation seems to give results fairly improved with respect to ones in column I, although they are still too low.

A second version investigated in [*10*] involves less drastic approximations; now the H.F. potential change is partially taken into account by retaining in Eq. (10) the terms in the summation corresponding to $k = j$, $m = l$. (In accordance with Ref. [*10*], we shall refer to this approximation as 'neglecting off-diagonal elements'). Eq. (8) now gives:

$$c_{lj}^{(1)} = \frac{\langle \Phi_l^{(0)} \mid h^{(1)} \mid \Phi_j^{(0)} \rangle}{(\varepsilon_j^{(0)} - \varepsilon_l^{(0)}) + \left[(\Phi_j^{(0)} \Phi_j^{(0)} \mid \Phi_l^{(0)} \Phi_l^{(0)}) - (\Phi_j^{(0)} \Phi_l^{(0)} \mid \Phi_j^{(0)} \Phi_l^{(0)}) \right]} . \tag{15}$$

By this approximation in conjunction with Eq. (7) we find results definitely improved and very close to the 'exact' version ones (columns III, IV).

As far as we know, there is not any evaluation of the magnetic observables of N_2 molecule, carried out in the perturbative SCF scheme. We have, therefore, extended the calculations to this molecule, in order further to investigate the kinds of approximations discussed in connection with LiH molecule. Our results for N_2 are too collected in table, and seem to confirm those obtained for LiH. The most noteworthy difference among the results for N_2 and LiH is to be found in the remarkable diversity of accuracy for the values of susceptibility and nuclear shielding constant. As a matter of fact, a rather good estimate of the paramagnetic contribution to the shielding constant is associated with a poor prevision in the analogous contribution to the susceptibility. Such a noticeable diversity of accuracy is likely due to the fact that the basis set used for N_2 is too restricted, and weighs, therefore, in an exceedingly different manner, operators associated with different observables.

We may also point out that the approximation which neglects the H.F. field modification, in the version presented in this paper, gives a different fraction of

Table

Calculation		I H. F. field perturb. neglected (ref. [*10*])	II H. F. field perturb. neglected (this paper)	III Off-diag. elements neglected (ref. [*10*])	IV Off-diag. elements neglected (this paper)	V Exact calculation	VI Experimental value
$\chi_{\mathrm{par}} \cdot 10^6$ (c.g.s. units)	LiH[a]	6.29	9.66	11.16	12.75	13.10	12.71 ∓ 0.04[d]
	N_2[b]	6.76	15.45	16.02	17.13	17.82	30.3[e]
$-\sigma_{\mathrm{par}} \cdot 10^6$	Li*H[c]	7.56	11.87	14.38	17.03	17.63	18.7 ∓ 1.2[d]
	N_2	158.7	263.2	383.4	438.8	459.5	482.3[d]

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[a] The calculations on LiH were performed using Ransil's BLMO basis set [*8*], and the following π basis [*10*]: $2p\,\pi$ (Li), $z = 2.53$; $3p\,\pi$ (Li), $z = 0.7057$; $2p\,\pi$ (H), $z = 0.91$; $3d\,\pi$ (Li), $z = 0.811$.

[b] N_2 calculations were performed using the minimal set of Ransil with Slater orbital exponent (SAMO) [*8*, *9*].

[c] Li* means that the nuclear magnetic shielding constant calculated is that of Li nucleus.

[d] See ref. [*10*]. [e] See ref. [*5*, *6*].

the 'exact' result as far as the two observables are concerned (see the table, columns II—V). So, while in the case of shielding constant the approximation gives about 60%, this value arises to about 80% for the susceptibility. The latter result seems to agree (within the limits of the very poor basis set chosen) with a remark by Kolker and Karplus [*5*]; according to it, large enough errors are to be expected, from neglecting H.F. field change, if low-energy excitations are dominating: for the magnetic shielding constant the perturbation operator weighs very heavily low-energy orbitals, making important the self-consistent correction.

Note added in proof. After our manuscript was sent for publication, we looked over a paper by P. W. Langhoff, M. Karpus and R. P. Hurst [J. chem. Physics **44**, 505 (1966)] dealing with a subject under many respects similar to that of our paper. The conclusions drawn by these authors about atomic systems do not seem in contrast with ours.

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