SECOND-ORDER PROPERTIES OF THE WATER MOLECULE

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The Karplus-Kolker uncoupled Hartree-Fock perturbation theory is applied to the calculation of the magnetic susceptibility and electric dipole polarizability of the water molecule from one-centre expanded Hartree-Fock molecular orbitals. The results obtained support some theoretically expected properties of the Karplus-Kolker variation-perturbation scheme.

In recent years much attention has been paid to the calculation of the so-called second-order molecular properties. The most frequently applied perturbed Hartree-Fock method [1, 2] requires a knowledge of a number of the excited-state wavefunctions. This difficulty can be circumvented in the variation-perturbation techniques [1, 3], *e.g.*, by using the so-called product approximation [3]

$$u_i^1 = f_i u_i^0$$

where u_i^1 is the first-order perturbed orbital, u_i^0 the unperturbed orbital and f_i the appropriate variation function.

The method developed by Karplus and Kolker [4] involves two further approximations. Neglecting the self-consistency conditions, *i.e.*, uncoupling, and omitting some terms which arise due to the non-local character of the Hartree-Fock Hamiltonian, one obtains a functional which does not include any two-electron integrals. On the other hand, the perturbed Hartree-Fock (PTHF) scheme requires the calculation of numerous two-electron integrals. A comparison of the Karplus-Kolker (KK) and PTHF schemes [5] shows that in the case of pure-imaginary perturbations the errors introduced by both approximations should almost cancel out each other. However, for real perturbing operators the KK results should differ significantly from the PTHF values. Calculations of atomic shielding factors and polarizabilities [6] support the theoretical analysis [5]. A quite similar relation between the KK and PTHF approaches is also expected for molecules.

In this note we shall study the second-order properties of the water molecule. We have chosen the paramagnetic part of the magnetic susceptibility (paramagnetic susceptibility) and the electric dipole polarizability as examples of the second-order properties

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related to a pure-imaginary and real perturbations, respectively. The molecule is placed in the yz plane and z is the symmetry axis.

The simplest molecular wavefunctions are the one-centre expanded (OCE) molecular orbitals. For the water molecule the OCE Hartree-Fock wavefunction has been calculated by Moccia [7] and gives good ground-state energy, dipole moment and diamagnetic part of the magnetic susceptibility. Moccia [8] evaluated also the dipole polarizability and the paramagnetic susceptibility using the PTHF method. This allows us to compare the present KK results with those obtained by a more advanced treatment.

The computational effort involved in the KK method depends on the choice of the variation functions f_i. It is convenient to choose f_i as a polynomial of an appropriate symmetry with the coefficients to be varied. Then, the min mization of the corresponding functional [4c] leads to a set of linear equations for these coefficients. This method has been utilized in the present study. Moreover, to estimate the convergence of the KK results we calculated both the paramagnetic susceptibility (χ^p) and electric dipole polarizability (α) with two variation functions each. In both cases the second function ($f^{II}_{i\lambda}$) included all the terms of the first one ($f^{I}_{i\lambda}$).

In the case of the paramagnetic susceptibility we have taken

$$f^{I}_{i\lambda} = a_{1i\lambda}x_\mu + a_{2i\lambda}x_\nu + a_{3i\lambda}x_\mu x_\nu$$

$$f^{II}_{i\lambda} = a_{1i\lambda}x_\mu + a_{2i\lambda}x_\nu + a_{3i\lambda}x_\mu x_\nu + a_{4i\lambda}x_\mu x_\nu^3 + a_{5i\lambda}x_\mu^3 x_\nu + a_{6i\lambda}x_\mu x_\nu x_\lambda^2$$

where $(\lambda, \mu, \nu) = (1, 2, 3)$ and the gauge origin is at oxygen.

The results obtained are compared with these of Moccia [8], with the susceptibilities calculated from the multicentre wavefunctions, and with experimental data.

TABLE I

Diamagnetic and paramagnetic contributions to the magnetic susceptibility tensor (in ppm · cgs)

	This work		Reference results			
	OCE KK–I	OCE KK–II	OCE PTHF [8]	STO[a] PTHF	STO[b] PTHF	Experiment [10]
χ^p_{xx}	1.434	1.582	1.909	1.993	2.076	2.33
χ^p_{yy}	0.499	0.602	0.641	1.825	0.444	0.79
χ^p_{zz}	0.310	0.327	0.876	2.520	0.849	1.40
χ^p_{Av}	0.748	0.837	1.139	2.113	1.123	1.51
χ^d_{xx}	−16.548	−16.548	−16.56	−16.971	−16.313	−16.0±1.8
χ^d_{yy}	−14.591	−14.591	−14.60	−13.407	−14.723	−12.9±1.6
χ^d_{zz}	−15.259	−15.259	−15.27	−15.361	−15.512	−14.9±2.0
χ^d_{Av}	−15.467	−15.467	−15.48	−15.246	−15.516	−14.6±2.0
χ_{tot}	−14.719	−14.630	−14.33	−13.133	−14.393	−13.1±2.0

[a] Calculated with the minimal basis set od Slater-type atomic orbitals (STO) [9].

[b] Extended STO basis set [9].

A comparison of the KK and PTHF results shows that in this case the agreement is rather satisfactory. The worst result was obtained for χ^p_{zz} for symmetry reasons and also due to the inaccuracy of the product approximation. It apears that if a richer variation function is used, the paramagnetic susceptibility should almost converge to the PTHF value.

The diamagnetic contribution to the magnetic susceptibility tensor is easily evaluated from the ground-state wavefunction. The calculated values are in good agreement with other theoretical results and coincide with those published by Moccia [8].

To evaluate the dipole polarizability we used one- and two-term variation functions:

$$f^{\mathrm{I}}_{ix} = b_{1ix}x, \quad f^{\mathrm{II}}_{ix} = b_{1ix}x + b_{2ix}xz$$

$$f^{\mathrm{I}}_{iy} = b_{1iy}y, \quad f^{\mathrm{II}}_{iy} = b_{1iy}y + b_{2iy}yz$$

$$f^{\mathrm{I}}_{iz} = f^{\mathrm{II}}_{iz} = b_{1iz}z$$

The convergence of the KK method was analysed in the work of Liebmann and Moskowitz [11], who calculated α using the LCGO (linear combination of Gaussian orbitals) wavefunction [12]. To obtain some information on the variation functions employed in this note, we compare our results (derived using the same LCGO function) with theirs.

TABLE II

Electric dipole polarizability (in 10^{-24} cm^3)

	OCE wavefunction			LCGO wavefunction			
	This work		PTHF [8]	This work		KK [11]	Experiment
	KK-I	KK-II		KK-I	KK-II		
α_{xx}	1.021	1.745	0.920	0.980	0.982	1.226	—
α_{yy}	1.483	1.632	1.202	1.375	1.413	1.651	—
α_{zz}	1.301	1.301	1.067	1.181	1.181	1.452	—
α_{tot}	1.268	1.559	1.063	1.178	1.192	1.443	1.45[a]

[a] Taken from Ref. [11].

It is evident that for the dipole polarizability the KK values do not converge to the PTHF results. A comparison of all the LCGO calculations shows that further improvement of the variation function would increase the difference between our OCE KK results and those of Moccia. A similar trend has also been noticed by Liebmann and Moskowitz [11]. In conclusion we may say that the performed calculations verify the general predictions concerning the KK scheme [5]. The obtained values of the paramagnetic susceptibility which correspond to a pure-imaginary perturbing operator, are in much better agreement with the PTHF results than the dipole polarizabilities. Thus, it can be expected that the method of Karplus and Kolker will give quite reliable results for any

pure imaginary perturbation provided a sufficiently flexible variation function f_i is used. On the other hand, for real perturbations appropriate corrections to the KK scheme [6] should be calculated.

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