A Variational Determination of Molecular Hyperpolarizabilities (*)

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Summary. — Expressions for the hyperpolarizabilities for second- and third-harmonic generations and for the induced Kerr effect are derived using a variation-perturbation method. This method requires only the wave function \( \Psi_0 \) of the ground state of the unperturbed molecule and yields the hyperpolarizability tensors, the components of which are determined by a variational calculus. By using a decomposition of the molecule into liges, we show that this method allows one to make calculations on complex molecules perturbed by static and dynamic electric fields.

1. - Introduction.

The effect of static and dynamic electric fields on atomic or molecular matter is to generate harmonics of different orders.

A semi-classical model for the interaction of electromagnetic radiation with atoms and molecules is used in this work.

To study the third-order phenomena of nonlinear optics, we determine the expressions for the hyperpolarizabilities appropriate to the generation of third harmonics and fundamentals' optical rectification and induced second-harmonic generation, the Kerr effect and the static hyperpolarizability.

We obtain these different expressions from a time-dependent variation-perturbation method similar to Karplus and Kolker's method (1) but using only the wave function of the ground state of the unperturbed system. With

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our variation-perturbation method we did not need to compute, as in other methods, all the eigenvalues of the Hamiltonian of the unperturbed system.

This method, which can lead to numerical results, had already given good results in magnetostatics (2,3) and in electro- and magneto-optics (4-7). For third-order phenomena of inert gases some interesting numerical values have already been published (8,9), but the development of the theory for the molecules was not given.

2. – General formalism.

2.1. Hamiltonian and wave function of the system. – We consider the system, atom or molecule in the Born-Oppenheimer approximation, perturbed by a monochromatic light beam \( E_\omega \), the frequency and vacuum wavelength of which are \( \omega \) and \( \lambda \).

The electric field of the light beam applied to the electronic centre of the system is

\[
E_\omega = E_\omega^0 \left[ \exp \{ i \omega t \} + \exp \{ - i \omega t \} \right].
\]

For induced second-harmonic generation, the Kerr effect and the static hyperpolarizability, the system is also perturbed by a static electric field \( E \).

The Hamiltonian of the system can be written as

\[
H = H^{(0)} - P \cdot (E + E_\omega).
\]

Before the perturbation was switched on, we assume that the molecule was in its ground state \( \Psi_0^{(0)} \). The wave function of the system, when the perturbation is switched on, is expanded in power series in the electric field. We write only the terms which are useful in this work:

\[
\Psi(R, t) = \Psi^{(0)}(R, t) + \Psi^{(1)}(R, t) + \Psi^{(2)}(R, t) + \Psi^{(3)}(R, t).
\]

The functions \( \Psi^{(1)}(R, t) \), \( \Psi^{(2)}(R, t) \) and \( \Psi^{(3)}(R, t) \) are the « steady-state

(3) YA. G. DORFMAN: Diamagnetism and the Chemical Bond (London, 1965).