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p-Character and the Polarizability of Molecular Hydrogen*

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The polarizability of molecular hydrogen has been calculated over a range of internuclear separations by Hartree-Fock perturbation theory, both coupled and uncoupled, using Gaussian functions as basis set. It is shown that a relatively simple function having the proper admixture of *s* and *p* character can yield polarizabilities comparable in accuracy with those obtained from highly sophisticated wavefunctions.

Die Polarisierbarkeit des Wasserstoffmoleküls wurde für einen Bereich von Kernabständen mit Hilfe der gekoppelten als auch der entkoppelten Hartree-Fock-Störungstheorie mit einer Basis von Gauss-Funktionen berechnet. Es wird gezeigt, daß eine relativ einfache Funktion mit der geeigneten Beimischung von *s*- und *p*-Charakter Polarisierbarkeiten ergibt, deren Genauigkeit solchen aus Rechnungen mit sehr komplizierten Wellenfunktionen vergleichbar ist.

Calcul de la polarisabilité de l'hydrogène moléculaire pour un éventail de distances internucléaires par la théorie des perturbations Hartree-Fock, couplée et non couplée, dans une base de fonctions gaussiennes. Une fonction relativement simple présentant un mélange convenable de caractère *s* et *p* fournit des polarisabilités, comparables au point de vue précision avec celles obtenues à partir de fonctions d'ondes très élaborées.

1. Introduction

As part of a wider program to study the effect of intermolecular forces on the polarizabilities of interacting molecules [1], we have undertaken a detailed investigation of the character of the wave-function in the treatment of two interacting H-atoms using Hartree-Fock perturbation theory both coupled and uncoupled. Hartree-Fock perturbation theory was first suggested by Dalgarno as a method of minimizing the error arising from the inaccuracy of the unperturbed wave function and applied by him to the polarization of atoms by electric and magnetic fields [2]. The coupled (CHF) and uncoupled (UHF) Hartree-Fock approximations of Dalgarno as well as other techniques were discussed by Cohen and Roothaan [3], by Langhoff, Karplus and by Hurst [4]; by Tuan, Epstein, and Hirschfelder [5] and by Musher [6a]. The method has been adapted to the treatment of electromagnetic properties of complex molecules, using LCAO-MO's to approximate the unperturbed wave-function, and applied to hydrocarbons [6b] and other polyatomic molecules [7]. The theory has recently been extended to the treatment of dynamic polarizabilities by the use of Padé Approximants [8].

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In all these methods, knowledge of a manifold of excited state is not required. Thus, accurate polarizabilities can now be computed with relative ease by a judicious choice of the basis set. The purpose of this paper is to discuss the importance of p-character in the computation of polarizabilities.

2. Procedure

The perturbed Hamiltonian H and wave function Ψ in the double perturbation theory [2, 9] are given by

$$H = H_0 + \lambda V + \mu W, \tag{1}$$

$$\Psi = \sum_{m,n} \lambda^m \mu^n \Psi^{(m,n)}, \tag{2}$$

where λV is the correction to the Hartree-Fock Hamiltonian H_0, and μW is the sum of one-electron operators $\mu\omega(i)$. The energy of the system E can then be expressed as

$$E = \sum_{n,m} \lambda^m \mu^n E^{(m,n)} \tag{3}$$

and the polarizability is given by [6b]

$$\begin{aligned} \alpha &= \mu^{-1}\left(\frac{\partial E}{\partial \mu}\right)_{\mu=0} = -2\sum_m \lambda^m E^{(m,2)} \\ &= \alpha^{(0)} + \alpha^{(1)} + \cdots \end{aligned} \tag{4}$$

where $\alpha^{(0)}$ is the zeroth order polarizability, $\alpha^{(1)}$ the first order polarizability etc. as defined by

$$\begin{aligned} \alpha^{(0)} &= -2E^{(0,2)} = -2\langle \Psi^{(0,0)} | W | \Psi^{(0,1)} \rangle \\ \alpha^{(1)} &= -2\lambda E^{(1,2)} = -2\lambda[\langle \Psi^{(0,1)} | V - E^{(1,0)} | \Psi^{(0,1)} \rangle \\ &\qquad + 2\langle \Psi^{(0,0)} | V - E^{(1,0)} | \Psi^{(0,2)} \rangle]. \end{aligned} \tag{5}$$

For a system with $2N$ electrons in the uncoupled Hartree-Fock scheme we have

$$\begin{aligned} \Psi_n^{(0,0)} &= \mathscr{A} u_1^{(0)}(1)\, u_2^{(0)}(2) \ldots u_{2N}^{(0)}(2N) \\ \Psi_n^{(0,1)} &= (E^{(0,0)} - H_0)^{-1} (1 - \mathcal{O}_n)(W - E_n^{(0,1)})\, \Psi_n^{(0,0)} \end{aligned} \tag{6}$$

$$= \sum_i \mathscr{A} u_1^{(0)}(1) u_2^{(0)}(2) \ldots u_i^{(1)}(i) \ldots u_{2N}^{(0)}(2N), \tag{7}$$

$$\begin{aligned} \Psi_n^{(0,2)} &= (E_n^{(0,0)} - H_0)^{-1} (1 - \mathcal{O}_n)(W - E_n^{(0,1)})(E_n^{(0,0)} - H_0)^{-1} (1 - \mathcal{O}_n)\, W \Psi_n^{(0,0)} \\ &= \sum_{i=1}^{2N} \mathscr{A} u_1^{(0)}(1)\, u_2^{(0)}(2) \ldots u_i^{(2)}(i) \ldots u_{2N}^{(0)}(2N) \\ &\quad + \sum_{i=1}^{2N-1} \sum_{j=i+1}^{2N} \mathscr{A} u_1^{(0)}(1)\, u_2^{(0)}(2) \ldots u_i^{(1)}(i) \ldots u_j^{(1)}(j) \ldots u_{2N}^{(0)}(2N) \end{aligned} \tag{8}$$

where $\mathcal{O}_n = |\Psi_n^{(0,0)}\rangle \langle \Psi_n^{(0,0)}|$.

If polarizability terms of order higher than $\alpha^{(1)}$ are neglected, the polarizability will depend only on $\{u_i^{(0)}\}$ and $\{u_i^{(1)}\}$, where $u_i^{(0)}$ and $u_i^{(1)}$ are the zeroth and first order one-electron spin orbitals respectively defined by [2, 10]

$$h(p)\,u_i^{(0)}(p)=e_i u_i^{(0)}(p) \tag{9}$$

and

$$\begin{aligned} u_i^{(1)}(p)&=[e_i-h(p)]^{-1}\,\omega(p)\,u_i^{(0)}(p)\\ &=\sum_{\substack{n\\(n\neq i)}}\frac{|u_n^{(0)}\rangle\,\langle u_n^{(0)}|}{e_i-e_n}\,\omega(p)\,u_i^{(0)}(p)\,. \end{aligned} \tag{10}$$

Expression (9) is the well known one-electron Hartree-Fock equation with e_i its orbital energy.

For a closed shell we obtain, on replacing the spin orbitals $\{u_i^{(0)}\}$ by the spatial orbitals $\{\phi_i\}$ [5],

$$\begin{aligned} \alpha^{(0)}&=-4\sum_{i=1}^{N}\langle\phi_i^{(0)}|\omega|\phi_i^{(1)}\rangle\\ \alpha^{(1)}&=-4\sum_{i,j}^{N}\{4\langle\phi_i^{(1)}\phi_i^{(0)}|\phi_j^{(1)}\phi_j^{(0)}\rangle-\langle\phi_i^{(1)}\phi_j^{(0)}|\phi_j^{(1)}\phi_i^{(0)}\rangle-\langle\phi_i^{(1)}\phi_j^{(1)}|\phi_i^{(0)}\phi_j^{(0)}\rangle\} \end{aligned} \tag{11}$$

where

$$\langle\phi_i^{(1)}\phi_i^{(0)}|\phi_j^{(1)}\phi_j^{(0)}\rangle=\iint\phi_i^{(1)}(1)\phi_i^{(0)}(1)\,\frac{1}{r_{12}}\,\phi_j^{(1)}(2)\,\phi_j^{(0)}(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

In the LCAO approximation with basis atomic orbitals given as $\boldsymbol{X}=\langle X_1,X_2,\ldots,X_M\rangle$, we have

$$\phi_k^{(0)}=\sum_r X_r C_{rk}^{(0)}\quad\text{and}\quad\phi_k^{(1)}=\sum_r X_r C_{rk}^{(1)}\,. \tag{12}$$

The zero-order linear coefficients. $\{C_{rk}^{(0)}\}$ are the solution of the Roothaan equation [11]

$$\boldsymbol{hC}=\boldsymbol{SCe} \tag{13}$$

where

$$h_{rs}=\langle X_r|h|X_s\rangle$$

and

$$\boldsymbol{S}=\boldsymbol{X}^{\dagger}\boldsymbol{X} \tag{14}$$

while the first order linear coefficients $\{C_{rk}^{(1)}\}$ can be obtained directly from the $\{C_{rk}^{(0)}\}$ according to the equation

$$C_{rj}^{(1)}=\sum_{\nu}^{\text{unocc}}\frac{\langle\phi_\nu^{(0)}|\omega|\phi_j^{(0)}\rangle}{e_j-e_\nu}\,C_{r\nu,\,j\varepsilon\text{occ}}^{(0)}\,. \tag{15}$$

If we define the unsymmetric density matrix

$$D_{\lambda p}=\sum_{j}^{\text{occ}}(C_{\lambda j}^{(0)}C_{pj}^{(1)}+C_{\lambda j}^{(1)}C_{pj}^{(0)}) \tag{16}$$

we have

$$\begin{aligned} \alpha^{(0)}&=-2\sum_{r,s}D_{rs}\langle X_r|\omega|X_s\rangle\,,\\ \alpha^{(1)}&=-2\sum_{r,s}D_{rs}G_{rs}\,,\\ \alpha&=\alpha^{(0)}+\alpha^{(1)}\,, \end{aligned} \tag{17}$$

where

$$G_{\mu\nu} = \sum_{\lambda,p} D_{\lambda,p}[2\langle X_\mu X_\nu | X_\lambda X_p\rangle - \langle X_\mu X_p | X_\lambda X_\nu\rangle]. \tag{18}$$

However, in the coupled Hartree-Fock method, the wave function Ψ is approximated by

$$\Psi = \mathscr{A} \prod_{i=1}^{2N} \{u_i^{(0)}(i) + u_i^{(1)}(i) + u_i^{(2)}(i) + \cdots\} \tag{19}$$

where $u_i^{(0)}$ is the Hartree-Fock solution and satisfies Eq. (9) while $u_i^{(1)}$ is the first order perturbed orbital which satisfies

$$u_i^{(1)} = (e_i - h)^{-1}[\omega + G - e_i^{(1)}]\, u_i^{(0)} \tag{20}$$

where G is a repulsion operator whose matrix element is defined by Eq. (18).

The first order linear coefficients $\{C_{ru}^{(1)}\}$ must now be determined iteratively according to Eq. (21),

$$C_{rj}^{(1)} = \sum_{v}^{\text{unocc}} \frac{\langle \phi_v^{(0)} | \omega + G | \phi_j^{(0)}\rangle}{e_j - e_v} C_{rv}^{(0)}, \quad j \varepsilon \text{occ} \tag{21}$$

and the polarizability is given by

$$\alpha = -2 \sum_{\lambda,p} D_{\lambda p} \langle X_\lambda | \omega | X_p\rangle. \tag{22}$$

3. Results and Discussion

The hydrogen molecule is chosen as an illustrative example to discuss the role of p-type functions in the computation of polarizabilities. If we assume the molecular axis of H_2 lies along the x axis, then the parallel component of the dipole polarizability $\alpha_{||}$ can be obtained from Eqs. (17) or (22) by setting ω equal to $-x$. Similarly, the perpendicular component of the dipole polarizability $\alpha_\perp$ can be obtained by setting ω equal to $-y$ or $-z$ and the mean polarizability is $(2\alpha_\perp + \alpha_{||})/3$.

The calculations were carried out for a wide range of internuclear separations, using Gaussian functions as basis sets. The exponential parameters were taken from Longstaff *et al.* [13] and Csizmadia *et al.* [12] for the free hydrogen atom. The polarizabilities at the equilibrium internuclear separation were computed for various choices of orbitals; the results are shown in Table 1. Table 2 lists the polarizabilities over a range of distances computed on the basis of a $2^s + 2^{p_x} + 2^{p_y}$ Gaussian set. Comparison of the equilibrium polarizability, calculated from the $2^s + 3^{p_x} + 3^{p_y}$ Gaussian basis set, with previously calculated results is made in Table 3.

It is seen from Tables 1 and 2 that, although the energy is largely dependent on the s character of the function, the polarizability is strongly affected by the choice of the p functions. Furthermore, it appears that $\alpha_{||}$ is dependent only on the s and p_x functions (x is the direction of the molecular axis), whereas $\alpha_\perp$ along the $y(z)$ direction depends on the s, p_x and $p_y(p_z)$ characters of the wave-function. Strengthening the p-character in a given direction will generally improve the component of polarizability in that direction but not necessarily the overall polarizability, α. The accuracy of the latter is apparently determined by a proper admixture of s, p_x and $p_y(p_z)$ character.

Table 1. *Polarizabilities*[a] *and energy of normal* H_2 *for different Gaussian basis sets. The polarizabilities were calculated by the use of uncoupled* (UHF) *and coupled* (CHF) *Hartree-Fock perturbation theory. The* $\alpha^{(0)}$ *and* $\alpha^{(1)}$ *are the zeroth and first order contributions respectively; the average polarizability is* $\alpha = 1/3(\alpha_{\|} + 2\alpha_{\perp})$. *All values are in atomic units*

	Basis	$2^s + 1^{p_x} + 3^{p_y}$	$2^s + 1^{p_x} + 2^{p_y}$	$2^s + 1^{p_x} + 1^{p_y}$	$2^s + 2^{p_x} + 3^{p_y}$	$2^s + 2^{p_x} + 2^{p_y}$	$2^s + 2^{p_x} + 1^{p_y}$	$2^s + 3^{p_x} + 3^{p_y}$	$2^s + 3^{p_x} + 2^{p_y}$	$2^s + 3^{p_x} + 1^{p_y}$
	$-E$	1.09434517	1.09434517	1.09434517	1.09487851	1.09487851	1.09087851	1.09087851	1.10108346	1.10108346
UHF	$\alpha_{\|}^{(0)}$	5.33904363	5.33904363	5.33904363	5.01211093	5.01211693	5.01211693	5.04630977	5.04630977	5.04640977
	$\alpha_{\|}^{(1)}$	1.12606240	1.12606240	1.12606240	1.08485051	1.08485051	1.08485051	1.20720877	1.20720877	1.20720877
	$\alpha_{\|}$	6.46510602	6.46510602	6.46510602	6.09696744	6.09696744	6.09696744	6.25351854	6.25351854	6.25351854
	$\alpha_{\perp}^{(0)}$	3.25854130	3.19208656	1.17468221	3.29911234	3.23455810	1.18971547	3.33445607	3.22045273	1.37091671
	$\alpha_{\perp}^{(1)}$	0.89279862	0.92575469	0.34302107	0.90049010	0.93469298	0.34759502	0.91516513	0.94490799	0.40084814
	$\alpha_{\perp}$	4.15733992	4.11784125	1.51770528	4.19960244	4.16925708	1.53731069	4.24862120	4.16536072	1.77176525
	α	4.92259529	4.9002628	3.16683750	4.83205740	4.81182320	3.05719610	4.91758690	4.86141330	3.26568300
CHF	$\alpha_{\|}$	6.84021856	6.84021856	6.84021856	6.48072845	6.48072848	6.48072845	6.71260869	6.71260869	6.71260869
	$\alpha_{\perp}$	4.50940622	4.50335976	1.65888292	4.55939394	4.55674777	1.68047895	4.61919644	4.56323884	1.93704863
	α	5.2863436	5.28231260	3.38599480	5.19983870	5.19807460	3.28056210	5.31700050	5.27969540	3.52890190

[a] Experimental values [14]: $\alpha_{\|} = 6.3$, $\alpha_{\perp} = 4.85$, $\alpha = 5.333$.

Table 2. *Polarizabilities and energy of interacting* H-*atoms at internuclear separation R in the uncoupled* (UHF) *and coupled* (CHF) *Hartree-Fock approximations computed from* $2^s + 2^{p_x} + 2^{p_y}$ *Gaussian basis set. Data in the last three rows are from other sources*

	$R(a_0)$	1.0	1.1	1.2	1.3	1.401	1.5	1.6	2.0	4.0
	$-E(au)$	1.03754102	1.06577040	1.08263647	1.09156405	1.09487851	1.09415450	1.09056478	1.06090117	0.88279354
UHF	$\alpha_{\parallel}^{(0)}$	3.23398140	3.61629351	4.03771577	4.50042981	5.01211693	5.55937266	6.16061410	9.11206292	47.5550366
	$\alpha_{\parallel}^{(1)}$	0.76799989	0.84338004	0.92161255	1.00202741	1.08485051	1.16702017	1.25034859	1.56296682	10.4522955
	$\alpha_{\parallel}$	4.00198129	4.45967355	4.95932833	5.50245722	6.09696744	6.72639283	7.41096268	10.6750297	37.1027411
	$\alpha_{\perp}^{(0)}$	2.44046132	2.63274512	2.82945745	3.02967137	3.23455810	3.43697893	3.64177496	4.43552095	7.03384604
	$\alpha_{\perp}^{(1)}$	0.68954025	0.74878066	0.80950703	0.87136131	0.93469298	0.99737092	1.06106630	1.31608409	2.38763991
	$\alpha_{\perp}$	3.13000157	3.38152578	3.63896448	3.90103268	4.16925108	4.43434985	4.70284126	5.75160504	9.42148595
	α	3.42066148	3.74090837	4.07908576	4.43484086	4.16925108	4.43434985	4.70284126	5.75160504	9.42148595
CHF	$\alpha_{\parallel}$	4.27872564	4.76289857	5.28912788	5.85906370	6.48072845	7.13675195	7.84808426	11.21439890	40.5998464
	$\alpha_{\perp}$	3.40568239	3.68395157	3.96900676	4.25937641	4.55674777	4.85091599	5.14926475	6.32374739	10.7291686
	α	3.69669681	4.04360057	4.40904713	4.79260551	5.19807460	5.61286131	6.04887125	7.95396456	20.6860611
	$\alpha_{\parallel}$	4.08782[a]	—	4.876[b]	5.451[b]	6.107[b]	6.862[b]	7.78072[a]	10.96438[a]	16.41833[a]
	$\alpha_{\perp}$	3.34102[a]	—	3.750[c]	4.067[c]	4.443[c]	4.870[c]	5.22760[a]	6.51086[a]	9.29535[a]
	α	3.58995[a]	—	4.125[b,c]	4.528[b,c]	4.998[b,c]	5.537[b,c]	6.07864[a]	7.99537[a]	11.66968[b,c]

[a] Results of Kolos *et al.* [20] using a 54 term expansion for the zeroth order wave function and a 34 term expansion for the first order correction function.

[b] Computed from ten terms James and Coolidge wave function [19].

[c] Computed from nine terms James and Coolidge wave function [19].

Table 3. *Comparison of the* H_2*-polarizabilities calculated for the equilibrium internuclear separation from* $3^s + 3^{p_x} + 3^{p_y}$ *Gaussian basis set with other sources. Different values under the same column heading represent different approximations*

	Das-Bersohn [15]	Hoyland [16]	Kolker-Karplus [17]	Kolos [20]	Ishiguro *et al.* [14]	This work	Experimental
$\alpha_{\parallel}$	16.57, 6.39, 5.71	8.00, 7.15	8.73	6.38049	6.107	6.713	6.3
$\alpha_{\perp}$	9.77, 4.64, 3.95	4.89, 4.70	5.41	4.57769	4.443	4.619	4.85
α	12.04, 5.22, 4.54	5.93, 5.52	6.52	5.17862	4.998	5.317	5.33

The computed polarizabilities at intermediate distances seem to be quite reasonable and are comparable with the results of Kolos *et al.* [20] and Ishiguro *et al.* [18]. However, the results at large distances are poor, probably because of the bad behavior of both the Gaussian basis functions and the Hartree-Fock equation. The most accurate values were obtained from the $2^s + 3^{p_x} + 3^{p_y}$ set, using CHF perturbation. The value 5.3170 a_0^3 for the equilibrium polarizability so obtained differs from the experimental value by only 0.3%. This degree of accuracy could not have been achieved on the basis of a purely *s* orbital determination. It is noteworthy that our calculations using only a simple eight term Gaussian set (but with the proper admixture of *s* and *p* character) can yield results which are as good as or better than the results obtain from very accurate and sophisticated wave-functions. This degree of accuracy is achieved only by the CHF method. The equilibrium α (see Table 2) obtained by the CHF method is better than the result of Ishiguro *et al.* [18]; the oposite is true when calculated by the UHF method.

We conclude that for the determination of polarizabilities the polarization of the basis functions is much more important than the number of basis functions.

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