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Polarizability in Excited States

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A linear response of a molecule in excited state to an external electric field is discussed in terms of frequency dependent polarizabilities. Results of accurate calculations of polarizabilities of the hydrogen molecule in its b $^3\Sigma_u^+$ and B $^1\Sigma_u^+$ states are presented. The results are compared with other *ab initio* and model calculations. It is shown that there is no contribution to the polarizability from the interaction of the b and B states with the states in which configuration $1\sigma_g\,3d\sigma_g$ or $1\sigma_g\,3d\pi$ predominates.

INTRODUCTION

The electric polarizability of a molecule is a measure of its ability to respond to an external electric field. Theoretically, this property is well defined in the sense that it is a measure of the additional dipole moment induced in a molecule by the field. For relatively weak fields the response of a molecular system to external perturbation is primarily linear. Nonlinear phenomena become more important for strong fields such as those produced by laser sources. The interaction of a molecule with relatively weak electric fields is well-described by perturbation theory. Calculations of the second order properties, such as polarizability, formally require knowledge of an infinite number of excited states (including the continuum), and therefore present formidable theoretical difficulties. These can be avoided by using the variation-perturbation technique.

The static polarizability of diatomic molecules in their ground states is one of the most frequently calculated molecular properties. Especially in the case of the hydrogen molecule a variety of different methods and wavefunctions were fused to evaluate this property (see for example ref.[1] and references therein). In contrast, very little is known on the polarizability of a molecule in its excited states, mostly because molecules in excited states usually have very short lifetimes. Consequently, the concentration of molecules in these states is very small and even the well-developed experimental methods cannot be applied. An exception are molecules in metastable excited states with sufficiently long lifetimes, where some of the methods may be used successfully. A possibility of determining polarizabilities in excited electronic states is based mostly on the effect of an electric field on electronic spectra, a phenomenon usually called the Stark effect. A review of the experimental methods determining polarizabilities of molecules in electronically excited states was given by Liptay.[2] The first experimental determination of excited state polarizability was carried out by Labhart on crocetindimethylester and bixindimethylester[3] from electrochromic absorption in solution. This type of investigation is limited mainly to the π-electron systems. For the hydrogen molecule, the only measurement of the excited state polarizability was performed by English and Kagann.[4] They used the molecular-beam magnetic-resonance to measure the Stark effect of the metastable c$^3\Pi_u$ electronic state and found the polarizability to be about 10^4 times greater that for the ground state.

The lack of experimental data on polarizabilities of molecules in electronically excited states causes small interest in the theoretical investigations of these properties. For conjugated hydrocarbons, calculations of excited state polarizabilities based on semiempirical methods were performed,[5-7] but the agreement of these theoretical results with the experimental data is only qualitative and in some cases there is no agreement at all.[6]

The most straightforward and the most reliable technique for calculating polarizabilities is direct *ab initio* computation. However, at present, the area of application of this technique is limited to small molecules, among which the hydrogen molecule is the best known example. The hydrogen molecule is a particularly important molecule since it has been used for testing new methods and it can serve as a model for other systems. For this molecule, very accurate theoretical results concerning the energy and molecular properties have been obtained, using explicitily correlated wavefunctions. For example the theoretical results of polarizability of the hydrogen molecule in its ground state agree with the experimental data within 0.1%.[8,9]

This work is essentially an extension of previous works concerned with the polarizability of the hydrogen molecule in ground state.[8,10,11] We consider here the polarizability for the b $^3\Sigma_u^+$ and B $^1\Sigma_u^+$ states of H_2.

THEORY

When a molecule is exposed to an external electric field, the interaction between the molecule and the field can be expanded in the form

$$H' = -\mu_\alpha F_\alpha - \frac{1}{3} Q_{\alpha\beta} F_{\alpha\beta} - \dots \tag{1}$$

where $\mu_\alpha = \sum_i e_i r_{i\alpha}$ is a component of the dipole moment operator, $Q_{\alpha\beta} = 1/2 \sum_i e_i (3 r_{i\alpha} r_{i\beta} - r_i \delta_{\alpha\beta})$ is a component of the quadrupole moment operator, F_α and $F_{\alpha\beta}$ are components of the electric field and the electric field gradient, respectively. The dipole moment of a molecule in the presence of the field is defined as a derivative of the average value of the energy with respect to the field

$$\mu_\alpha = -\frac{\partial E}{\partial F_\alpha} = \mu_\alpha^\circ + \alpha_{\alpha\beta} F_\beta + \frac{1}{2} \beta_{\alpha\beta\gamma} F_\beta F_\gamma + \dots \tag{2}$$

where μ° is the permanent dipole moment and the other terms in (2) describe the changes in the dipole moment induced by the field. For H_2, the permanent electric dipole moment μ° is absent. The leading term describing the interaction with the electric field is the linear polarizability α. Higher terms, called hyperpolarizabilities, are important only in the case when a strong field is applied. We shall concentrate here on the linear polarizability. Therefore, we can neglect higher terms in expansion (1) and we start with the Hamiltonian in which the perturbation is limited to the term containing the dipole moment operator. In the laboratory fixed reference system this Hamiltonian has the form

$$H = H^{\circ} - \sum_{\alpha} \sum_{i} e_i r_{i\alpha} F_{\alpha} \tag{3}$$

H° stands for the Hamiltonian of a molecule in the absence of the field, e_i is the charge of the i-th particle, r_i stands for its vector. The rigous transformation from the laboratory system to the molecular internal system leads in this case to separation of the translation motion without any approximation, *i. e.* there is no coupling term[12,13] and the internal Hamiltonian has the form

$$H = H_{\mathrm{mol}} + H_{\mathrm{nad}} + H_{\mathrm{int}} \tag{4}$$

The first term in (4) is the internal molecular Hamiltonian of familiar form and the second term appears as a result of separation of the translational motion for the isolated molecule.[14] This term is responsible for the so-called nonadiabatic effects. The perturbation term, the dipole moment operator in the internal reference system, is defined as[13]

$$H_{\mathrm{int}} = [\frac{q}{2M} [(M_{\mathrm{a}} - M_{\mathrm{b}}) - \frac{1}{2} (Z_{\mathrm{a}} - Z_{\mathrm{b}})] R + (\frac{q}{M} + 1) \sum_{i} \mathbf{r}_i] \mathbf{F} \tag{5}$$

where M_a, M_b, Z_a, Z_b are the masses and charges of the nuclei and q and M are the total charge and mass of a molecule. R stands for the internuclear vector and $\mathbf{r}_i$ is the radius vector of the i-th electron measured from the geometrical centre of the nuclei. It is seen from (5) that the correction terms to the dipole moment operator are of the order of M^{-1} and exist only for charged molecules.

In the presence of time-dependent perturbation, *i. e.* an oscillatory electromagnetic field with angular frequency ω, the perturbation term is of the form

$$H_{\mathrm{int}} = (e^{i\omega t} + e^{-i\omega t}) \mathbf{F} \vec{\mu} \tag{6}$$

and to determine the frequency-dependent polarizability $\alpha(\omega)$, the time-dependent Schrödinger equation (7) must be used

$$i \frac{\partial \Psi(r, t)}{\partial t} = (H^{\circ} + H_{\mathrm{int}}) \Psi(r, t) \tag{7}$$

By expanding $\Psi(r, t)$ in powers of F, the first-order correction to the wave-function, $\Psi^1(r, \omega, t)$ can be shown to have the form

$$\Psi^1(r, \omega, t) = \Psi_+^{\ 1}(r, \omega)\, e^{i(\omega - E^{\circ})t} + \Psi_-^{\ 1}(r, \omega)\, e^{-i(\omega - E^{\circ})t} \tag{8}$$

and $\Psi^1_{\pm}(r, \omega)$ must satisfy the first order equation

$$(H^{\circ} - E^{\circ} \pm \omega) \Psi^1_{\pm}(r, \omega) = -\mu_F \Psi^{\circ}(r) \tag{9}$$

$\Psi^\circ (r)$ and E° stand for, respectively, the eigenfunction and the eigenvalue of the unperturbed Schrödinger equation

$$(H^\circ - E^\circ)\, \Psi^\circ (r) = 0 \tag{10}$$

and $\mu_F = \mu \mathbf{F}/F$. The frequency dependent polarizability is then determined as an integral of the form

$$\alpha_{\pm} (\omega) = -\frac{1}{2} \langle \Psi^1_{\pm} (r, \omega) \,|\, \mu_F \,|\, \Psi^\circ (r) \rangle \tag{11}$$

METHOD OF COMPUTATION

The calculation of the polarizability tensor has been the subject of much theoretical research and variety of methods have been proposed (see for example refs. [1, 15, 16] and references therein). In this work we use the variation-perturbation method, *i. e.* we calculate the polarizability by applying variation procedure to the first-order equation (9) in order to obtain the first-order function. The unperturbed and the first-order functions have been assumed to be linear expansion

$$\Psi^\circ = \sum_n c_n \varphi_n{}^\circ \tag{12}$$

$$\Psi^1 = \sum_n b_n \varphi_n{}^1 \tag{13}$$

The variation condition for the first-order equation leads to the inhomogeneous set of linear equations for coefficient b_n

$$\sum_i [H_{in}{}^\circ - (S_{in} E^\circ \pm \omega)]\, b_n = -\langle \varphi_n{}^1 \,|\, \mu_F \,|\, \Psi^\circ \rangle \tag{14}$$

where

$$H_{in} = \langle \varphi_i{}^1 \,|\, H^\circ \,|\, \varphi_n{}^1 \rangle$$
$$S_{in} = \langle \varphi_i{}^1 \,|\, \varphi_n{}^1 \rangle \tag{15}$$

Having coefficients b_n, the values of polarizability can be obtained from the formula

$$\alpha (\omega) = \sum_i b_i \langle \varphi_i{}^1 \,|\, \mu_F \,|\, \Psi^\circ \rangle \tag{16}$$

For the hydrogen molecule there are only two nonzero independent components of the polarizability tensor *viz.* $\alpha = \alpha_{xx} = \alpha_{yy}$ the perpendicular component and $\alpha_{||} = \alpha_{zz}$ the parallel component. The average polarizability is then defined as

$$\alpha (\omega) = \frac{1}{3} [\alpha_{||} (\omega) + 2\alpha_{\perp} (\omega)] \tag{17}$$

and its anisotropy as

$$\gamma (\omega) = \alpha_{||} (\omega) - \alpha_{\perp} (\omega) \tag{18}$$

The basis functions in eqs. (12 and (13) for both unperturbed Ψ° and perturbed Ψ^1 functions were expressed in terms of the elliptic coordinates (ζ, η, φ)

$$\varphi_n = \varphi_n (1, 2) \pm \varphi_n (2, 1) \tag{19}$$

and

$$\varphi_n(1,2) = e^{-\alpha\zeta_1-\alpha\zeta_2}\,\zeta_1^{k_n}\,\eta_1^{l_n}\,\zeta_2^{m_n}\,\eta_2^{p_n}\,[e^{\beta\eta_1+\beta\eta_2} +$$

$$+ (-1)^{l_n+p_n+1}\,e^{-\beta\eta_1-\beta\eta_2}]\,[(\zeta_1^2-1)(1-\eta_1^2)]^{s/2}\,e^{i(\varphi_1-\varphi_2)s/2}\,\varrho^{u_n} \tag{20}$$

where α, β, α and β are variational parameters, $\rho = 2r_{12}/R$ with r_{12} and R the interelectronic and internuclear distances, respectively, k_n, l_n, m_n, p_n and u_n are integers greater than or equal to zero. The sign in (19) is positive for the singlet state and negative for the triplet state. For $s = 0$ and $p = 0$ Eq. (20) represents the Σ_g^+ state, $s = 0$ and $p = 1$ the Σ_u^+ state and for $s = 1$ and $p = 1$ Eq. (20) represents the Π_g state.

Computations were performed separately for the perpendicular and parallel components of the polarizability tensor. The Born-Oppenheimer approximation bas been assumed in this paper and the resulting polarizabilities have been given as functions of the internuclear distance.

POLARIZABILITY FOR THE b $^3\Sigma_u^+$ STATE

The hydrogen molecule in its lowest triplet state is the simplest nonbonded molecular system for which, in contrast to larger systems, very accurate calculations can be carried out. Therefore, it can serve as a model when studying the collision-induced phenomena for lightly bound dimers or van der Waals' molecules.

Polarizabilities for atoms and molecules are modified by collisions and this effect is accessible to measurements of some optical properties of compressed inert gases. For two interacting atoms this effect is described by the polarizability anisotropy γ, $\gamma(R) = \alpha_{\parallel}(R) - \alpha_{\perp}(R)$ and the trace of the pair contribution to the polarizability defined as

$$\mathrm{Tr}\,\Delta\,\alpha(R) = \Delta\,\alpha_{\parallel}(R) + 2\,\Delta\,\alpha_{\perp}(R) \tag{21}$$

where

$$\Delta\,\alpha_{\parallel}(R) = \alpha_{\parallel}(R) - 2\,\alpha_o$$

$$\Delta\,\alpha_{\perp}(R) = \alpha_{\perp}(R) - 2\alpha_o \tag{22}$$

and $2\,\alpha_o$ is the polarizability of the two noninteracting atoms. The polarizability anisotropy γ causes depolarization and is related to field-induced birefringence (Kerr effect). An extensive review of the subject of collision induced polarizability of diatomic systems is given by Frommhold.[17]

The trace of the pair contribution to the polarizability $Tr\,\Delta\alpha(R)$ is obtained as the difference of two quantities which are very nearly equal for intermediate and large values of R. Therefore, numerical precision is important in calculations of this property. For example, in the finite field calculations, with field strengths of 0.001 a. u., convergence of the density matrix to one part in 10^6 or 10^7 is required.[18] This accuracy can be achieved, however, only for small molecular systems and accurate *ab initio* calculations of pair polarizabilities of noble gas diatomics have thus been limited to He_2[19] Several models have been, therefore, developed for this type of calculations. The simplest model is the dipole-induced-dipole (DID) model introduced by Silberstein[20] in which

$$\alpha_{\|}(R) = 2\,\alpha_o = 4\,\alpha_o^2 R^{-3} + 8\,\alpha_o^3 R^{-6} + \ldots \tag{23}$$

$$\alpha_{\perp}(R) = 2\,\alpha_o - 2\,\alpha_o^2 R^{-3} + 2\,\alpha_o^3 R^{-6} + \ldots \tag{24}$$

A number of other models incorporating overlap effects and exchange contribution have been developed.[21-23]

The first calculation of the polarizability of the hydrogen molecule in the lowest triplet state was performed by DuPre and McTague.[24] They calculated $\alpha_{\|}$ and $\alpha_{\perp}$ from the approximate formulas obtained by the variation-perturbation method

$$\alpha_{\|} = 8\,[\langle z_1^2\rangle + \langle z_1 z_2\rangle]^2$$
$$\alpha_{\perp} = 8\,[\langle x_1^2\rangle + \langle x_1 x_2\rangle]^2 \tag{25}$$

and using the Hirschfelder-Linnett wavefunction. In (25), z_i and x_i are coordinates of the i-th electron with z coordinates along the internuclear axis. It has been shown[8] that, in the case of polarizability for the ground state of H_2, formulas (25) lead to an error of about 10% when correlated wavefunctions of type (20) are used to evaluate the expectation values. For the triplet state, DuPre and McTague found $\alpha_{\|}$ to be less than $\alpha_{\perp}$ for internuclear distances R of 7 to 10 a. u. whereas the true result is opposite. Moreover, they obtained the asymptotic value of polarizability to be 8 a. u., as opposed to the exact value of 9 a. u.

More recently, the electron gas model was applied by Cina and Harris[25] to evaluate the polarizabilities for the triplet state in the region of internuclear distance R, $1.0 \leq R \leq 10.0$ a. u. For larger values of R, between 4.0 and 12.0 a. u. Hunt and Buckingham[18] performed *ab initio* calculations using a large basis set and the finite field method. They calculated $\Delta\,\alpha_{\|}$ and $\Delta\,\alpha_{\perp}$ using restricted Hatree-Fock (RHF) and configuration interaction (CI) methods and compared the results with predictions of several models. The above mentioned calculations concerned the static polarizability, *i. e.* for $\omega = 0$. Recently, the dynamic polarizabilities have been calculated.[26,27] In these calculations, the variation-perturbation method and explicitly correlated wavefunctions of type (20) were used. The unperturbed wavefunction Ψ° consisted of 60 terms in expansion.[12] This wavefunction gives the energy for the triplet state only by about 0.02 cm^{-1} higher than than the best values calculated by Kołos and Wolniewicz[28] for intermediate and large internuclear distances. The first order functions of the $^3\Sigma_g^+$ symmetry, used to derive the parallel component, and those of the $^3\Pi_g$ symmetry, used for the calculations of perpendicular component, consisted of 45 terms in the expansion (13). In Figure 1, the components of the static polarizability tensor as functions of R for the b $^3\Sigma_u^+$ state are displayed and compared with the corresponding curves for the ground state.[11] It is seen that these curves are considerably different for these two states in the region of small R. This difference is caused by different united atom limits for these states. The b state tends to the $^3P(1s2p)$ state of helium whereas the ground state tends to the $^1S(1s1s)$ state of helium. For $R \Rightarrow \infty$, the components of polarizability for the b state approach the same limits as those for the ground state; the parallel components approach the asymptotic limit from above whereas the perpendicular ones from below. The inflection point on the $\alpha_{\perp}$ curve for the b state is clearly due to contraction of the electronic cloud near $R = 2.5$ a.u. along the z axis in contrast to the ground state where expansion of the electronic cloud is observed with a maximum near 3.3 a. u.[29,30]

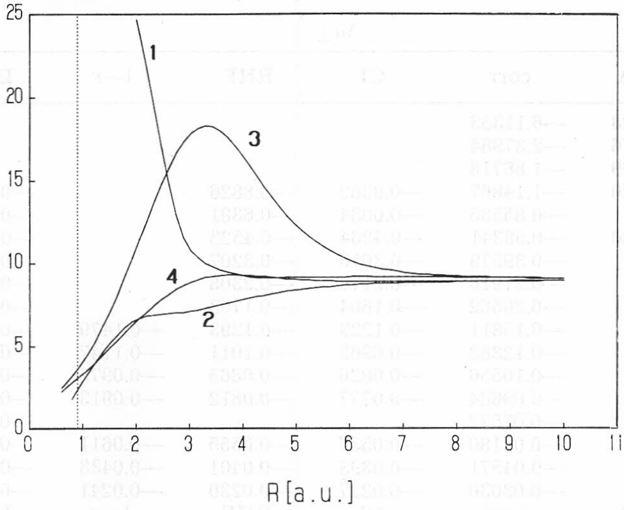

Figure 1. The components of the static polarizability $\alpha_{\|}$ and $\alpha_{\perp}$ for the b $^3\Sigma_u^+$ state (curves 1 and 2) as compared with the corresponding quantities for the ground state (3 and 4).

In Table I, a comparison is made with the previous results for the components of static polarizability for the b state. We compare here the results of the electron gas model (EGA) of Cina and Harris,[25] first-order DID (DID-1) and second-order DID (DID-2) values, results of restricted Hartree-Fock (RHF) and the configuration interaction (CI) methods of Hunt and Buckingham,[18] of the long-range model $(l - r)$[18,31] and the results obtained with the explicitly correlated wavefunction.[26,27] It is clear that the electron gas model results represent very poorly the behaviour of the polarizability components as functions of R. There are significant differences between our values and RHF and CI results. They differ for R near the van der Waals minimum by 22% (CI) and 18% (RHF) for perpendicular component. These differences become much larger for smaller R. For $R = 4.0$ a.u. the differences are 6% (CI), 45% (RHF), and 27% (CI), 23% (RHF) for $\alpha_{\|}$ and $\alpha_{\perp}$, respectively. For $\alpha_{\perp}$, these differences increase slightly for increasing R. As a result, the trace of the pair polarizability, which is sensitive to the quality of function used in the calculations, is negative for large R when calculated with the explicitly correlated wavefunction ($Tr\Delta\alpha\,(R = 12) = -0.0129$ a. u.) whereas the CI result is positive ($Tr\Delta\alpha\,(R = 12) = 0.0024$ a. u.).

The model values of $\alpha_{\perp}$ differ from our values by 8% $(l - r)$ and 20% (DID) near the van der Waals minimum and by 5% $(l - r)$ and 11% (DID) for $R = 10.0$ a. u. respectively, while the agreement for the parallel component is slightly better. It is worth noting that the $\alpha_{\perp}$ values obtained from the long-range model approximate accurate values (corr) much better than those calculated from CI. Consequently, the polarizability anisotropy obtained from

TABLE I

The components of polarizability tensors $\Delta\alpha_{\parallel}$ and $\Delta\alpha_{\perp}$ for H_2 in the triplet state. Results from the electron gas model (EGA), correlated wavefunction calculations (corr), CI and RHF calculations and from the first-order DID (DID1), second-order DID (DID2) and long-range (l—r) models

$\Delta\alpha_{\perp}$

R	EGA	corr	CI	RHF	l—r	DID1	DID2
1.0	—0.888	—6.11353					
2.0	—0.476	—2.37984					
3.0	—0.699	—1.86718					
4.0	—0.520	—1.14867	—0.8362	—0.8826		—0.6328	—0.5884
4.5		—0.85535	—0.6034	—0.6381		—0.4444	—0.4225
5.0	—0.380	—0.58341	—0.4264	—0.4523		—0.3240	—0.3123
5.5		—0.39579	—0.3016	—0.3207		—0.2434	—0.2368
6.0		—0.27918	—0.2170	—0.2308		—0.1875	—0.1836
6.7		—0.20582	—0.1604	—0.1703		—0.1474	—0.1450
7.0		—0.15811	—0.1223	—0.1293	—0.1479	—0.1181	—0.1166
7.5		—0.12382	—0.0962	—0.1011	—0.1147	—0.0960	—0.0950
7.85		—0.10556	—0.0826	—0.0865	—0.0975	—0.0837	—0.0829
8.0		—0.09684	—0.0777	—0.0812	—0.0913	—0.0791	—0.0784
8.5		—0.07572				—0.0660	—0.0655
9.0		—0.06180	—0.0537	—0.0555	—0.0611	—0.0556	—0.0553
10.0		—0.04571	—0.0393	—0.0401	—0.0433	—0.0405	—0.0403
12.0		—0.03030	—0.0227	—0.0230	—0.0241	—0.0234	—0.0233
R	EGA	corr	CI	RHF	l—r	DID1	DID2
				$\Delta\alpha_{\parallel}$			
1.0	—0.864	5454.07					
2.0	0.489	15.7325					
3.0	0.290	1.8392					
4.0	0.328	0.25894	0.2762	0.1409		1.2656	1.4436
4.5		0.17016	0.1802	0.0790		0.8889	0.9767
5.0	0.371	0.16902	0.1829	0.1067		0.6480	0.6947
5.5		0.19469	0.2029	0.1461		0.4868	0.5131
6.0		0.20773	0.2127	0.1713		0.3750	0.3906
6.0		0.20529	0.2080	0.1785		0.2948	0.3045
7.0		0.19136	0.1928	0.1722	0.2292	0.2362	0.2423
7.5		0.17165	0.1723	0.1582	0.1874	0.1920	0.1961
7.85		0.15680	0.1570	0.1464	0.1639	0.1674	0.1705
8.0		0.15038	0.1505	0.1311	0.1550	0.1582	0.1610
8.5		0.13064				0.1319	0.1338
9.0		0.11238	0.1119	0.1077	0.1096	0.1111	0.1125
10.0		0.08322	0.0828	0.0810	0.0802	0.0810	0.0817
12.0		0.04767	0.0478	0.0473	0.0468	0.0469	0.0471

the long-range model gives the best agreement with the anisotropy calculated from explicite correlated wavefunctions (see Table II), which can be considered the most accurate result so far.

In Table II, we compare the polarizability anisotropy obtained from different methods as the function of internuclear distance R. It is well established from the studies of collision induced polarizabilities for light inert gases[32] that at SCF (or RHF) level the long-range polarizability anisotropy γ approaches the DID value calculated with the SCF polarizability, as expected. Electron correlation increases the anisotropy and at the van der

TABLE II

The polarizability anisotropy (in a. u.) for H_2 in the triplet state

R	γ_{RHF}	γ_{CI}	γ_{corr}	γ_{DID1}	γ_{DID2}	$\gamma_{\text{l–r}}$
6.0	0.4021	0.4297	0.48691	0.5625	0.5742	
6.5	0.3428	0.3684	0.41111	0.4424	0.4495	
7.0	0.3015	0.3151	0.34947	0.3542	0.3589	0.3771
7.5	0.2593	0.2685	0.29547	0.2880	0.2911	0.3021
7.85	0.2329	0.2396	0.26236	0.2512	0.2534	0.2614
8.0	0.2223	0.2282	0.24722	0.2373	0.2394	0.2463
9.0	0.1632	0.1656	0.17418	0.1667	0.1678	0.1707
10.0	0.1211	0.1220	0.12893	0.1215	0.1220	0.1235
12.0	0.0703	0.0705	0.07800	0.0703	0.0704	0.0709

Waals minimum the polarizability anisotropy falls below the DID value calculated with α^{CI} by 6% for H . . . H,[18] 10% for He . . . He[19,33] and 20% for Ne . . . Ne.[34,35] This conclusion is in contrast to our finding. The anisotropies with explicitly correlated wavefunction are larger than DID values for $R > 7$ a. u. and for $R = 12.0$ a. u. the anisotropy is larger by about 10% than the anisotropy obtained from all other methods listed in Table II. This conclusion together with the obtained positive value of the trace of the collision induced polarizability for large R may be useful for a better understanding of the collision induced phenomena.

The components of dynamic polarizability as functions of frequency ω, calculated using the explicitly correlated wavefunctions,[26,27] are shown graphically in Figures 2 and 3 for two internuclear distances $R = 2.0$ and $R = 6.0$ a. u. The dynamic polarizabilities $\alpha_{\parallel}(R)$ possess singularity points, which similarly to the ground state, are clearly due to the interaction of the b state with the states of the ${}^3\Sigma_g^+$ symmetry in the presence of an electric field. The singularity point appears when ω is equal to the difference of the adiabatic energy between the b state and the given state which can be mixed in by the field. For $\alpha_{\parallel}(R = 1.5)$ and $\alpha_{\parallel}(R = 2.0)$, the first pole appears in the region $\omega = 0.0834 — 0.1$ a. u. and $\omega = 0.1535 — 0.1655$ a. u.,[27] respectively, and the energy gap between the b and the closest a ${}^3\Sigma_g^+$ state is 0.0855 a. u. for $R = 1.5$ and 0.1610 a. u. for $R = 2.0$ a. u., respectively.[28,36,37] The second pole appears as a result of interaction of the b state with higher states of the ${}^3\Sigma_g^+$ symmetry. The next states, above the a state, *viz.* the h and g states, lie above the b state by, respectively, 0.1675 and 0.1710 a. u. for $R = 1.5$ a. u. and 0.2369 and 0.2378 for $R = 2.0$ a. u.[32,39] However, the region of ω, where the second pole appears, is $\omega = 0.225$—0.2354 a. u. for $R = 1.5$ a. u. and $\omega = 0.3$—0.325 a. u. for $R = 2.0$ a. u.,[26,27] respectively, *i. e.* much larger than the corresponding energy gaps. This means that there is no contribution to the polarizability form the interaction of the b state with the h and g states. It is worth noting that in the vicinity of the equilibrium the h and g states can be described as a mixture of $1s\sigma_g\,3s\sigma_g$ and $1s\sigma_g\,3d\sigma_g$ configurations.

For the perpendicular component there are no poles although the b state can be mixed in by the field with the i ${}^3\Pi_g$ state. The lack of pole in this case can be explained by the character of the i state for small and intermediate values of R. For this region of internuclear distances the i state can be described as $1\sigma_g\,3d\pi$ with a promoted outer orbital. This configuration is

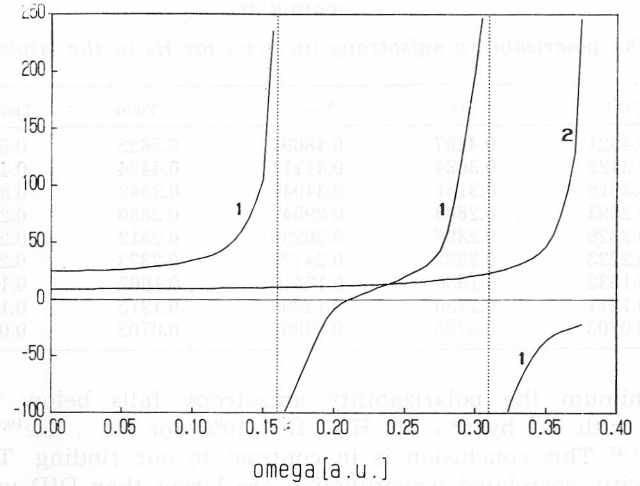

Figure 2. The parallel component of $\alpha(\omega, R)$ for the b state at $R = 2.0$ a. u. (1) and $R = 6.0$ a. u. (2) plotted as functions of field frequency ω. Broken lines denote the positions of the poles.

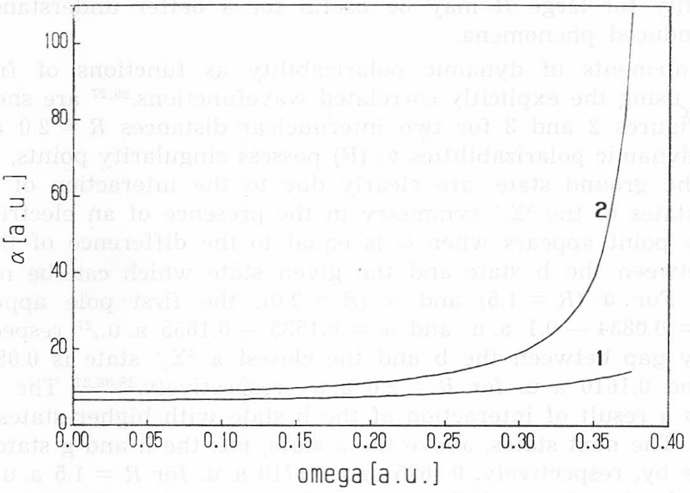

Figure 3. The perpendicular component of $\alpha(\omega, R)$ for the b state at $R = 2.0$ a. u. (1) and $R = 6.0$ a. u. (2) plotted as functions of field frequency ω.

predominant for $R < 6.0$ a. u.[40] Therefore, we can conclude that configurations $3d\pi$ and $3d\sigma$ are responsible for the lack of interaction between the b state and the h and g $^3\Sigma_g^+$ states (in the case of $\alpha_{\|}(\omega)$) and the i $^3\Pi_g$ state (in the case of $\alpha_{\perp}(\omega)$).

POLARIZABILITY FOR THE B $^1\Sigma_u^+$ STATE

In this section the results of calculations of $\alpha_{\|}(\omega)$ and α (ω) for the B $^1\Sigma_u^+$ state of H_2 for its equilibrium geometry, similar to that for the b $^3\Sigma_u^+$ state, are presented. Calculations were performed using functions of the type of eq. (20) consisting of 70 terms in expansion (12) for the unperturbed function, and 60 terms in expansion (13) for the perturbed unction of the ${}^1\Sigma_g^+$ symmetry for the calculations of parallel component and of the ${}^1\Pi_g$ symmetry for the calculations of perpendicular component. The results are listed in Table III and displayed graphically in Figures 4 and 5. The value of static polarizability for the B state is much larger than that obtained for the ground state, being almost 40 times larger for the parallel component and 10 times larger in the case of the perpendicular component. It mirrors the difference in discplacements of electrons from the internuclear axis which are much bigger in the B state.[41,42] The dominant contribution to the polarizability $\alpha_{||}$ of the B state comes from the interaction with the E, F ${}^1\Sigma_g^+$ state in the presence of the field. The first pole that appears in Figure 4 is clearly due to the above mentioned interaction. The energy difference between the B and the E, F states for $R = 2.43$ a. u. is 0.04897 a. u.[43,44] whereas the region of ω where the pole appears is between 0.045 and 0.05 a. u. The higher singularity points appear for $\omega = 0.11 - 0.115$ and for $\omega = 0.12 - 0.14$ a. u. The energy gaps between the B state and the posible interacting higher states, *i. e.* the G, K and H, H, are 0.1010 and 0.1097 a. u., respectively. The G, K state can be described for small R as predominantly a $1s\sigma_g\,3d\sigma_g$ state and, therefore, according to the conclusion from the former section does not contribute to the polarizability. Accordingly, the second pole can be attributed to the interaction with the H, H state, which for small R is described as $1s\sigma_g\,3s\sigma_g$.

For the perpendicular component the singularity point appears at $\omega = 0.12 - 0.14$ a. u. whereas the energy gap between the B state and the lowest state of ${}^1\Pi_g$ symmetry, *i. e.* the I state, amounts to 0.1032 a. u.[40,43] The I state can be described similarly as the i state by the $1s\sigma_g\,3d\pi$ configuration and, therefore, does not contribute to the polarizability of the B state.

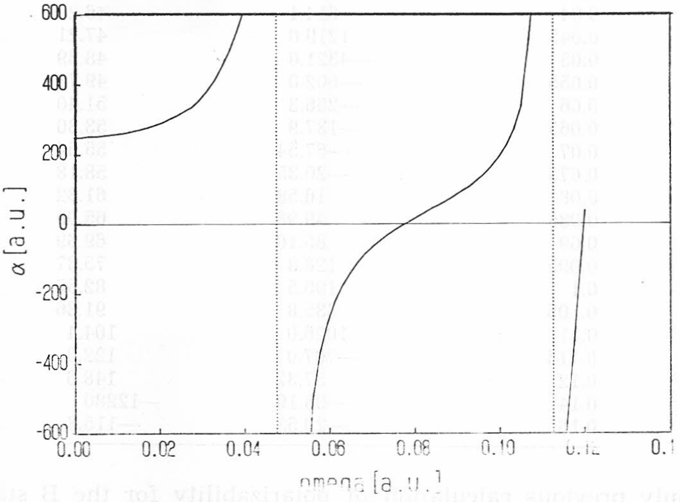

Figure 4. The parallel component of $\alpha(\omega, R)$ for the B state at $R = 2.43$ a. u. plotted as function of ω. The broken lines denote the positions of the poles.

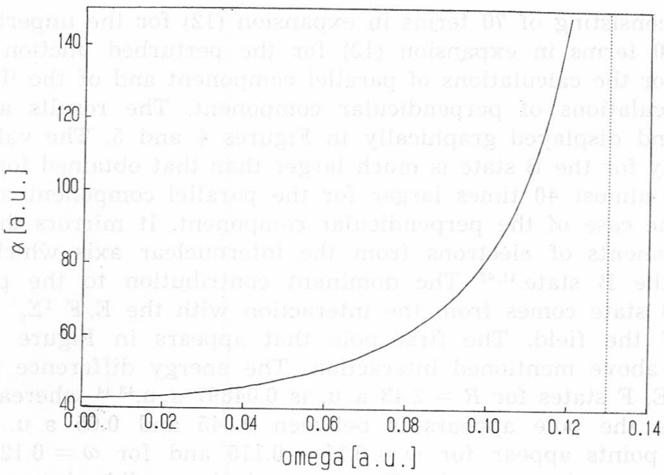

Figure 5. The perpendicular component of $\alpha(\omega, R)$ for the B state at $R = 2.43$ a.u. plotted as function of ω.

TABLE III

Paralell $\alpha_{||}$ *and perpendicular* $\alpha_{\perp}$ *components of dynamic polarizability for the B* $^1\Sigma_u^+$ *state at selected field frequencies* ω *(all values in a.u.)*

ω	$\alpha_{\|\|}$	$\alpha_{\perp}$
0.0	249.7	42.80
0.0004	249.8	42.80
0.001	249.8	42.80
0.005	250.5	42.85
0.01	258.0	43.00
0.02	287.3	43.60
0.03	361.0	44.64
0.04	614.1	46.20
0.045	1219.0	47.21
0.05	—4321.0	48.39
0.055	—602.0	49.78
0.06	—266.3	51.40
0.065	—137.9	53.30
0.07	—67.54	55.54
0.075	—20.35	58.18
0.08	16.58	61.32
0.085	49.98	65.09
0.09	85.10	69.69
0.095	128.8	75.37
0.1	195.5	82.55
0.105	335.8	91.86
0.11	1026.0	104.4
0.115	—707.0	122.0
0.12	37.32	148.6
0.14	—96.19	—12280
0.16	—20.53	—115.3

The only previous calculation of polarizability for the B state was performed by Grimes *et al.*[45] using the Hartree-Fock and configuration interaction wavefunctions and the finite-field methods. They calculated both the parallel and the perpendicular components of static polarizability for a single internuclear distance $R = 2.43$ a. u. which is the equilibrium distance for the B state. In Table IV we compare their values with the results reported here in this paper. The differences between these values are similar to those found for the b state and it is clear from these differences that the perpendicular component is more difficult to calculate accurately.

TABLE IV

The parallel and perpendicular components of polarizability tensor (in a. u.) for the B state of H_2 ($R = 2.43$ a. u.)

Function	$\alpha_{\perp}$	Δ%	$\alpha_{\parallel}$	Δ%
SCF	338	35	67	56
CI	257	3	50	17
corr	249.7		42.80	

The hydrogen molecule in its B state is of particular interest since, as it was found by Farantos *et al.*,[46] it forms a chemically bonded system with helium atom in its ground state. The minimum at 0.0558 a. u. of the potential energy curve corresponds to an angle of 45° between the H—H bond vector R and the vector r locating He relative to the centre of mass of H_2 for $R = 4.0$ a. u. and $r = 1.5$ a. u. The existence of the bound excited state for this system near an avoided crossing with the ground state of the same symmetry can explain the strong electronic quenching of HD ($B\,^1\Sigma_u^+$, $v = 3$, $J = 2$) in collision with He (^1S) observed by Fink *et al.*[47] The nature of bonding in the H_2 ($B\,^1\Sigma_u^+$) + He (^1S) system has been discussed by Nicolaides and Zdetsis[48] in terms of simple electrostatic interactions. The results presented here can give an insight into the nature of long-range interactions since the polarizability of the B state contributes to these interactions in terms R^{-6} and R^{-8}. It was shown that the quadrupole moment of the B state vanishes for the equilibrium geometry of the $(H_2He)^*$ system[12] and thus it reduces the attraction part of the long-range potential. Also, the parallel component of polarizability decreases when the internuclear distance R increases in the vicinity of equilibrium for the B state.[1] These factors favour the charge transfer leading to the formation of the H^- (1s2s) + HeH^+ system.

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Polarizabilnost u pobuđenim stanjima

Jacek Rychlewski

Razmatran je linearni odziv molekule u pobuđenom stanju, izložene djelovanju vanjskoga električnog polja. Izračunana je frekvencijski ovisna polarizabilnost H_2 molekule u pobuđenim stanjima $b\,^3\Sigma_u^+$ i $B\,^1\Sigma_u^+$ i uspoređena s drugim *ab initio* i modelnim proračunima.