Ab initio Study of Some Excited States of AlH

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The propagator approach yields excitation energies (polarization propagator) and ionization potentials (electron propagator) without the computation of separate ground state and final state wavefunctions and is well suited for studying dynamical properties. These methods are applied to AlH molecule: excitation energies, ionization potential, optical and generalized oscillator strengths.

Key words: Electron and polarization propagators – Dynamical properties of diatomic molecule: AlH.

1. Introduction

In a previous paper, we used the Polarization Propagator theory to the study of the inelastic electron impact cross section of some atoms. This theory provides a suitable means of calculation for dynamical properties [1].

In this work, we present results about excited states, Optical Oscillator Strengths (OOS) and Generalized Oscillator Strengths (GOS) of the AlH molecule. The excited states of AlH have not been studied theoretically very well up to now. The interest of this study lies especially in astrophysics since the emission lines of AlH appear in the Solar Spectra [2] and some stars like χ Cygni [3].

2. Description of Electronic Excited States and Ionization by Propagators Technic

These methods have been widely described these last years [4, 5, 6]. In the notation of the super operator formalism [7], the spectral representation of the

Polarization and the electron Propagator becomes, after partitioning [8]

$$\langle\langle bb^+\rangle\rangle_E^{-1} = (h_2|E\hat{I} - \hat{H}|h_2) - (h_2|\hat{H}|h_4)\times(h_4|E\hat{I} - \hat{H}|h_4)^{-1}\times(h_4|\hat{H}|h_2) \tag{1}$$

where

$$|h_2\rangle = a_m^+ a_\gamma \tag{2a}$$

$$|h_4\rangle = a_m^+ a_n^+ a_\gamma a_\delta \tag{2b}$$

for the Polarization Propagator and

$$|h_2\rangle = a_\gamma \tag{3a}$$

$$|h_4\rangle = a_n^+ a_\gamma a_\delta \tag{3b}$$

for the Electron Propagator. Greek indices refer to occupied spin orbitals and latin indices to virtual ones. a_i^+ and a_j are respectively the Dirac creation and annihilation operators. The first order approximation is obtained by neglecting the h_4 part of these projectors bases. The matrix representations can be found in [19] for the Polarization Propagator and in [20] for the Electron Propagator, the ground state being introduced by the Rayleigh–Schrödinger perturbation of the Hartree–Fock ground state.

The poles of the Propagator Eq. (1) correspond to the ionization potential for the Electron Propagator and to the transitions energies for the Polarization Propagator. This one can be represented in its diagonal form as follows [9]:

$$\langle\langle b;b^+\rangle\rangle_E = \begin{Bmatrix} Z(E) & Y(E) \\ Y(E) & Z(E) \end{Bmatrix} \begin{Bmatrix} (E1-\omega(E))^{-1} & 0 \\ 0 & -(E1-\omega(E))^{-1} \end{Bmatrix}$$

$$\times \begin{Bmatrix} Z^+(E) & Y^+(E) \\ Y^+(E) & Z^+(E) \end{Bmatrix} \tag{4}$$

$Z(E)$ and $Y(E)$ are eigenvectors of Eq. (5).

The residue for a pole is:

$$\text{Res}(E_n) = \begin{Bmatrix} \Gamma_n Z(E_n)Z^+(E_n) & \Gamma_n Y(E_n)Z^+(E_n) \\ \Gamma_n Z(E_n)Y^+(E_n) & \Gamma_n Y(E_n)Y^+(E_n) \end{Bmatrix} \tag{5}$$

with

$$\Gamma_n^{-1} = \left(1 - \frac{d}{dE}\omega_n(E)\right)E = E_n. \tag{6}$$

The matrix element of any mono-electronic operator M between an excited state $|n\rangle$ and the ground state $|0\rangle$ is given by:

$$|\langle 0|M|n\rangle|^2 = \sum_{\substack{i(m\gamma) \\ j(p\delta)}} \langle p|M|\delta\rangle[Z(E_n)_{jn}Z^+(E_n)_{ni} + Y(E_n)_{jn}Y^+(E_n)_{ni}$$

$$+ 2Z(E_n)_{jn}Y^+(E_n)_{ni}]\langle m|M|\gamma\rangle\Gamma_n. \tag{7}$$

3. The Generalized Oscillator Strength (GOS)

The GOS is an important property of atoms and molecules. It represents the system response to an excitation. It is directly related to the differential Born cross section.

If ΔE_n is the transition energy from the ground state $|0\rangle$ to the excited state $|n\rangle$, R and a_0 respectively the Rydberg and the Bohr radius, the GOS is defined by [10]:

$$f_n(K) = \frac{\Delta E_n}{R(Ka_0)^2} |\varepsilon_n(K)|^2 \tag{8}$$

where K is the momentum transfer and $\varepsilon_n(K)$ the form factor for a molecular system of Z electrons and M nuclei.

$$\varepsilon_n(K) = \int \psi_n^* \sum_{j=1}^{Z} \exp(iK \cdot r_j) \psi_0 \, d^3r_1 \cdots d^3r_Z \, d^3R_1 \cdots d^3R_M. \tag{9}$$

ψ_0 and ψ_n are the ground and excited state eigenfunctions of the molecule; r_i and R_j are the electronic and nuclear coordinates.

If we neglect the rotational structure and within the Born–Oppenheimer approximation, the GOS must be summed over all final rotational states and averaged over all initial rotational states what leads to average over molecular orientations.

We shall not consider explicitly the vibrational levels. Then, the expression of the averaged GOS becomes [11]:

$$f_n(K) = \frac{\Delta E_n}{R(a_0 K)^2} \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \left[\langle n| \sum_{j=1}^{Z} \exp(iK \cdot r_j)|0\rangle \right]^2 \cdot \sin\theta \, d\theta \, d\phi \tag{10}$$

$|n\rangle$ and $|0\rangle$ being the electronic parts of the total wave functions ψ_n and ψ_0, θ and ϕ are the Euler angles between a system of coordinates fixed in the molecule and a space-fixed frame.

For a diatomic molecule, the scalar product $K \cdot r_j$ is independent of ϕ and the integration is straightforward. The θ integration is performed using Gauss–Newton quadrature.

When the Born approximation is valid, the GOS $f_n(K)$ approaches the Optical Oscillator Strength as K goes to zero. The expression of the OOS in the dipole length approximation is: [12]

$$F_n = \tfrac{2}{3}[\langle n|r|0\rangle]^2 \Delta E_n. \tag{11}$$

4. Transition Energies

The SCF calculation for the ground state of AlH molecule was performed using a double ζ STO basis on each atom augmented by a set of polarization orbitals $3d$ on Al and $2p$ on H (Table 1). The molecular orbital eigenvalues are collected in Table 2. They are in good agreement with Cade et al. calculations [13].

$1s_{Al} = 14.2269$	$1s'_{Al} = 10.7261$
$2s_{Al} = 5.0036$	$2s'_{Al} = 3.6312$
$3s_{Al} = 1.7739$	$3s'_{Al} = 1.1077$
$2p_{Al} = 7.2078$	$2p'_{Al} = 3.6541$
$3p_{Al} = 1.6827$	$3p'_{Al} = 0.9138$
$1s_H = 0.9962$	$1s'_H = 1.3500$
$2s_H = 1.6815$	$2p'_H = 1.3301$
$3d_{Al} = 1.3719$	

Table 1. STO basis set for the ground state AlH calculation

Table 2. SCF molecular orbital eigenvalues for AlH

MO	ε (a.u.)	MO	ε (a.u.)
1σ	−58.4880	8σ	0.4557
2σ	−4.9003	4π	0.5118
1π	−3.2094	9σ	0.6755
3σ	−3.2081	10σ	0.8458
4σ	−0.4968	5π	1.0446
5σ	−0.2886	11σ	1.0893
2π	0.0333	12σ	4.6399
6σ	0.1736	13σ	5.6957
7σ	0.3338	6π	10.0348
3π	0.4444	14σ	10.5217
		15σ	97.6033

The value of the first ionization potential, evaluated by means of the Electron Propagator: 0.2915 a.u. is identical with the result of Grimaldi [14]. The Electronic transition energies for the $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ transitions are calculated to the first and second order and compared in table 3.

The corresponding OOS is evaluated with help of the second order results by equation (7) in which the operator $M = r$ (dipole length approximation). The

Table 3. Excitation energies (a.u.) and OOS

		1st order	2nd order	exp.	Grimaldi	OOS
$1\,^3\Pi$	$(5\sigma \rightarrow 2\pi)$	Unstable	Unstable	a	0.054	
$1\,^1\Pi$	$(5\sigma \rightarrow 2\pi)$	0.1125	0.1144	0.1069 [15]	0.1184	0.184
$2\,^3\Pi$	$(4\sigma \rightarrow 2\pi)$	0.2552	0.2576	$a + 0.1683$ [16]	0.2250	
$2\,^1\Pi$	$(4\sigma \rightarrow 2\pi)$	0.3224	0.3266		0.2314	0.812
$3\,^3\Pi$	$(3\sigma \rightarrow 2\pi)$	2.9192	2.9292			
$3\,^1\Pi$	$(3\sigma \rightarrow 2\pi)$	2.9172	2.9312			0.001
$1\,^3\Sigma$	$(5\sigma \rightarrow 6\sigma)$	0.1977	0.1885		0.1922	
$1\,^1\Sigma$	$(5\sigma \rightarrow 6\sigma)$	0.2864	0.2770	0.2031 [17]	0.2013	3.581
$2\,^3\Sigma$	$(4\sigma \rightarrow 6\sigma)$	0.3995	0.3869			
$2\,^1\Sigma$	$(4\sigma \rightarrow 6\sigma)$	0.4629	0.4358			8.037
$3\,^3\Sigma$	$(3\sigma \rightarrow 6\sigma)$	3.0950	3.0844			
$3\,^1\Sigma$	$(3\sigma \rightarrow 6\sigma)$	3.0928	3.0864			0.995

corresponding integration was realized analytically by a Fourier-transform method described by Avery et al. [18]. To every order of approximation the $1\,^3\Pi$ pole remains too close to zero (0.009 a.u.). Considering the number of iterations and diagonalizations to be carried out, this value appears unreliable. But this feature affects slightly the behaviour of the other poles because to each pole corresponds a different numerical matrix to be diagonalized. We can observe that practically for all transitions, the difference between the singulet and the triplet energies is very weak, especially for the $3\,^3\Sigma$ and $3\,^1\Sigma$ states. We see that the excitation energies for the $1\,^1\Pi(5\sigma \to 2\pi)$, $1\,^1\Sigma(5\sigma \to 6\sigma)$ and the $2\,^3\Pi(4\sigma \to 2\pi)$ states agree well with the calculation of [14]. But this is not true for the $1\,^1\Sigma(5\sigma \to 6\sigma)$ and the $2\,^1\Pi(4\sigma \to 2\pi)$. The reason is that these two levels are Rydberg states and our basis is too limited to describe them. Supplementary diffuse orbitals would have been introduced.

The highest values of OOS correspond to the $1\,^1\Sigma$ and $2\,^1\Sigma$ states, whereas the $3\,^1\Sigma$ one is quite small. We must underline that the $3\,^1\Pi$, $2\,^1\Sigma$ and $3\,^1\Sigma$ levels lie above the first ionization potential.

5. The GOS $f_n(K)$

The evaluation of the matrix element $\langle \chi_a | \exp(iK \cdot r) | \chi_b \rangle$ referred to as Fourier transforms of the distribution $\chi_a^+ \chi_b$, has been detailed elsewhere [19]. The $|\varepsilon_n(K)|^2$ values averaged over all molecular orientations are given in Table 4.

The θ-integration was performed using 9-points quadrature. All the functions $|\varepsilon_n(K, \theta)|^2$ fall to a minimum near $\theta = \pi/2$ as shown in Fig. 1 for the $1\,^1\Sigma$ and $1\,^1\Pi$ transitions.

The curves of the figs 2 and 3 (corresponding to the Table 4) present a maximum whereas the $2\,^1\pi$, $2\,^1\Sigma$ and $3\,^1\Sigma$ curves are regularly decreasing. The function

Table 4. $\varepsilon_n(K)^2$ in a.u.

K^2	$1\,^1\Pi$	$2\,^1\Pi$	$1\,^1\Sigma$	$2\,^1\Sigma$	$3\,^1\Sigma$
0.01	0.06936	0.13995	0.10081	0.52670	0.20920
0.0225	0.08011	0.13725	0.12498	0.52539	0.20893
0.04	0.09376	0.13365	0.15577	0.52344	0.20856
0.0576	0.10595	0.12998	0.18341	0.52134	0.20818
0.09	0.12478	0.12313	0.22641	0.51714	0.20750
0.16	0.15229	0.10882	0.29024	0.50679	0.20603
0.25	0.16829	0.09065	0.32903	0.49145	0.20547
0.36	0.16928	0.07166	0.33415	0.47053	0.20202
0.64	0.13392	0.03359	0.25884	0.41233	0.19677
1.00	0.08044	0.01724	0.14412	0.33841	0.19056
1.44	0.03853	0.00798	0.06373	0.26031	0.18353
1.96	0.01533	0.00444	0.03403	0.18907	0.17633
3.24	0.00202	0.00179	0.04620	0.08795	0.16130
4.84	0.00301	0.00133	0.05591	0.03798	0.14713
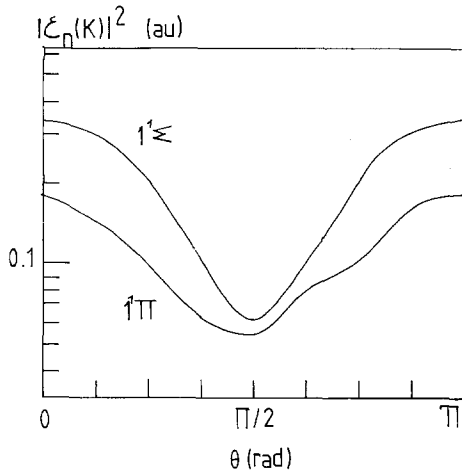
Fig. 1. Modulus of the form factor as a function of the incident angle θ for $k^2 = 0.04$ a.u
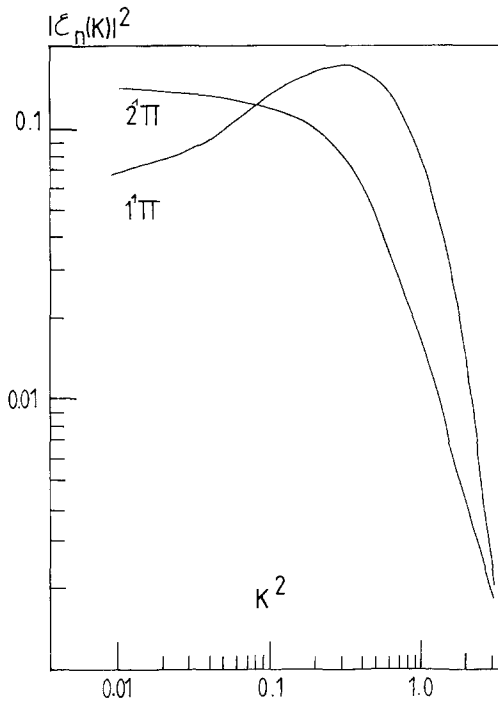
Fig. 2. Modulus of the form factor for the $\sigma \to \pi$ transitions. All quantities are expressed in atomic units

for the $3\,^1\Sigma$ state is always quasi zero. The $3\,^1\pi$ curve is not drawn because it corresponds to a transition too high in the continuum.

6. Conclusion

We have discussed calculations on the excited states of AlH molecule including the computation of generalized and optical oscillator strengths as an application
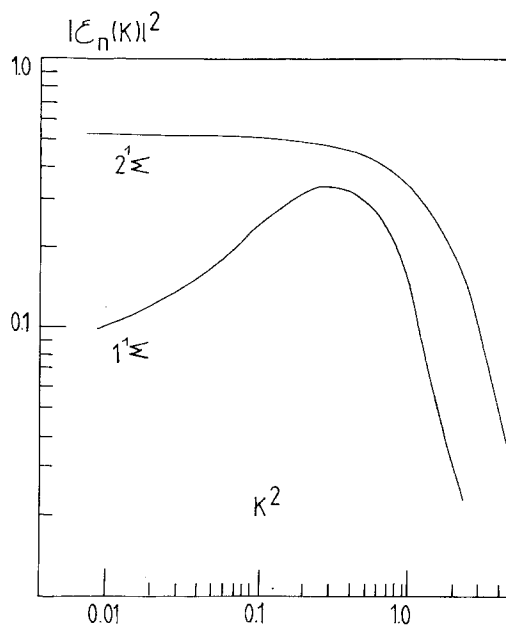
Fig. 3. Modulus of the form factor for the $\sigma \to \sigma$ transitions

of the Propagators method. The electronic transition energies agree with the experimental results except for the Rydberg states for which our orbital basis is too restricted.

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