

PHYSICAL REVIEW LETTERS

VOLUME 27

18 OCTOBER 1971

NUMBER 16

Direct Sum-of-States Calculations of the Frequency-Dependent Polarizability of H₂

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(Received 19 July 1971)

The direct sum-over-states method of calculation of dynamic polarizabilities is used to compute the most accurate values for the frequency-dependent polarizability of the ground state yet obtained by *ab initio* calculations. Accurate values of Rayleigh depolarization ratios are also obtained. A Rayleigh depolarization ratio for Lyman- α radiation (unpolarized light) of 0.0562 is obtained. The feasibility of direct computation of the electric dipole components of the resolvent operator for molecules is established.

We report in this paper calculations for the frequency-dependent polarizability of H₂ based on the direct use of the sum-over-states definitions,

$$\alpha_{\parallel}(\omega) = 3 \sum_n f_{0n}'' / [(E_n - E_0)^2 - \omega^2], \quad (1)$$

$$\alpha_{\perp}(\omega) = \frac{3}{2} \sum_n f_{0n}' / [(E_n - E_0)^2 - \omega^2]. \quad (2)$$

Comparison can be made with experimental values of refractive indices¹ and Rayleigh depolarization ratios.^{2,3} The $\alpha(\omega)$ values reported here appear to be the most accurate yet obtained for H₂ by direct calculation. For Lyman- α radiation we calculate a Rayleigh depolarization ratio [for unpolarized light, ρ defined by Eq. (9)] of 0.0562, in comparison with a previous semiempirical value³ of 0.055, and a Rayleigh scattering cross section of 2.28 cm². The significance of the work reported here, however, lies more in the implication that an accurate representation of an ap-

proximate resolvent operator

$$(E_0 - \sqrt{H_0})^{-1} = \sum_{i \neq k}^n \frac{|\Psi_i\rangle \langle \Psi_i|}{E_0 - E_i} \quad (3)$$

can be obtained for molecules, rather than in the actual results for H₂ presented. The availability of accurate approximate resolvent operators will allow calculations of the interaction of molecules with radiation, nuclear spin-spin interaction, magnetic susceptibility, and other molecular properties.

The set of wave functions used in these calculations was obtained by the use of standard configuration interaction programs for molecular wave functions, and extension of this work to other systems is straightforward. Note that the set of molecular wave functions Ψ_i used in Eqs. (1)–(3) are, in this formulation, the N -particle total wave functions, not one-particle orbitals. Similarly the E_i are total electronic energies rather than orbital energies.

Previous *ab initio* calculations of the dynamic polarizabilities of H_2 have used time-dependent Hartree-Fock perturbation theory⁴⁻⁸ or many-body perturbation theory.^{9,10} Dalgarno and Williams¹¹ and, more accurately and extensively, Dalgarno and Victor¹ have constructed a semi-empirical model of the dipole spectrum from which they obtain polarizabilities using equations similar to (1) and (2). Langhoff and Karplus¹² have used a technique based on Padé approximants to extrapolate long-wavelength refractivity data into the far ultraviolet. Accurate variational calculations of the static polarizability have been reported by Kołos and Wolniewicz.¹³

The crux of the method reported here lies in the calculation of a set of molecular states which is numerically complete in the domain spanned by the set of states connected to the ground state of H_2 by dipole transitions. A knowledge of these states and energies is equivalent to the calculation of the ${}^1\Pi_u$ and ${}^1\Sigma_u^+$ components of the resolvent operator in a particular domain. It has been shown by Dalgarno and Epstein¹⁴ that on constraining the form of an expansion basis for a set of wave functions

$$\Psi_i = \sum_j c_{ij} \Phi_j, \quad i = 1 \cdots n, \quad (4)$$

such that the set Φ_j contains the product of the perturbing operator and the ground-state wave function Ψ_0 , sum rules analogous to and including the oscillator-strength sum rule are satisfied by sets of wave functions derived by conventional variational calculations. This provides us with a means of obtaining a set of molecular-state wave functions that satisfy sum rules closely related to the sum rules of (1) and (2). Our results suggest that near exact satisfaction of a few sum rules leads to others such as (1) and (2)

being well satisfied. The effective oscillator strengths $f_{0n}({}^1\Sigma_g^+ \rightarrow n{}^1\Sigma_u^+)$, $f_{0n}({}^1\Sigma_g^+ \rightarrow n{}^1\Pi_u)$ used in our application of Eqs. (1) and (2) were calculated with various sets of expansion functions for the ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ states ranging up to 52 configurations and ground-state (${}^1\Sigma_g^+$)-state wave functions of from 14 to 24 configurations. Taking the perturbing operator to be the dipole length transition operator and using for Ψ_0 the accurate variationally computed approximation to the ground-state wave function, we find that the oscillator-strength sum rule and several other sum rules are very accurately satisfied by our approximate set of wave functions. Table I compares calculated values for some sum rules, the exact values, and accurate values from related expectation values computed by Kołos and Wolniewicz.^{13,15} The calculated values shown in Table I were obtained using a 14-configuration ground-state ${}^1\Sigma_u^+$ -state wave function and a 26-configuration ${}^1\Pi_u$ -state wave function.

The parallel and perpendicular polarizabilities are related to experiment via the average polarizability

$$\alpha(\omega) = \frac{1}{3}[\alpha_{\parallel}(\omega) + 2\alpha_{\perp}(\omega)] \quad (5)$$

and the anisotropy

$$\gamma(\omega) = \alpha_{\parallel}(\omega) - \alpha_{\perp}(\omega). \quad (6)$$

The depolarization ratio for polarized incident light and observation in a direction perpendicular to the incident light of Rayleigh-scattered (incident and scattered frequency identical) light only is³

$$\rho_v^c(\omega) = \frac{3}{4}\gamma^2(\omega)/[45\alpha^2(\omega) + \gamma^2(\omega)], \quad (7)$$

while ρ_v^t , the depolarization ratio for observation

TABLE I. Sum rules: $S^{\parallel}(k) = 3\sum_n f_n^{\parallel}(E_n - E_0)^k$, $S^{\perp}(k) = \frac{3}{2}\sum_n f_n^{\perp}(E_n - E_0)^k$.

	$R = 1.0a_0$	$R = 1.4a_0$	$R = 2.0a_0$
$S^{\parallel}(0) = \text{number of electrons}$	2.00 (2.00) ^a	1.99 (2.00) ^a	2.00 (2.00) ^a
$S^{\parallel}(-1) = 2\langle\psi_0 (x_1 + x_2)^2 \psi_0\rangle$	1.37 (1.36) ^b	1.72 (1.73) ^b	2.28 (2.28) ^b
$S^{\parallel}(-2) = \alpha^{\parallel}(\omega = 0)$	4.10 (4.09) ^c	6.35 (6.38) ^c	10.9 (11.0) ^c
$S^{\perp}(0) = \text{number of electrons}$	2.00 (2.00) ^a	2.00 (2.00) ^a	2.00 (2.00) ^a
$S^{\perp}(-1) = 2\langle\psi_0 (x_1 + x_2)^2 \psi_0\rangle$	1.20 (1.20) ^b	1.70 (1.70) ^b	1.98 (1.98) ^b
$S^{\perp}(-2) = \alpha^{\perp}(\omega = 0)$	3.34 (3.34) ^c	6.53 (6.51) ^c	8.84 (8.85) ^c

^aThe value in parenthesis is the exact value.

^bThe value in parenthesis is the value obtained by W. Kołos and L. Wolniewicz, Ref. 15.

^cThe value in parenthesis is the value obtained by W. Kołos and L. Wolniewicz, Ref. 13.

TABLE II. Polarizability and refractive index.

λ (Å)	$\alpha(\omega)^a$	$\alpha(\omega)^b$	$(n-1) \times 10^4{}^a$	$(n-1) \times 10^4{}^b$	$\alpha(\omega)^c$	$\alpha(\omega)^d$
∞	5.414	5.437	1.355	1.360	5.372	5.226
6328.0	5.519	5.554	1.381	1.390	5.472	5.322
2968.1	5.929	5.960	1.483	1.491	5.856	5.698
1854.6	7.010	7.035	1.754	1.760	6.846	6.667
1215.7	12.556	12.2	3.141	3.05	12.07	11.167

^aThis calculation.

^bExperimental, as quoted in Ref. 1.

^cThese are values for a single internuclear separation, $R=1.40$, Ref. 9.

^dThese are values for a single internuclear separation, $R=1.40$, Ref. 7.

of Rayleigh- and rotational Raman-scattered lines, is³

$$\rho_v^t(\omega) = 3\gamma^2 / [45\alpha^2(\omega) + 4\gamma^2(\omega)]. \quad (8)$$

The depolarization ratio for unpolarized incident light is³

$$\rho(\omega) = 6\gamma^2(\omega) / [45\alpha^2(\omega) + 7\gamma^2(\omega)]. \quad (9)$$

The index of refraction $n(\omega)$ of a gas is related to the average polarizability by

$$n = 2\pi N\alpha(\omega) + 1, \quad (10)$$

where N is Avogadro's number.

Table II compares our calculated indices of refraction with the experimental values as quoted by Dalgarno and Victor¹ and some previous calculations for several wavelengths. The calculated values of $\alpha(\omega)$ and $\gamma(\omega)$ quoted in Table II and elsewhere in this paper are averaged over vibrational and rotational motion with weight factors for a temperature of $T=293^\circ\text{K}$. The value of the index of refraction quoted here for Lyman- α radiation is that of Gill and Heddle¹⁶ (GH). The experiments of GH yield n through a proportionality to the depolarization ratio

$$(n-1)^2 \propto [6 - 7\rho(\omega)] / [6 + 6\rho(\omega)];$$

GH used $\rho=0.014$. We have corrected the n value of GH by using our value of $\rho(1217.5 \text{ Å})=0.0562$. The agreement between calculation and experiment here is not as precise as at other frequencies. This may be because the absolute values quoted by GH depend on a rather old value of ρ for N_2 .

Rowell, Aval, and Barrett³ (RAB) have made what appear to be extremely precise measurements of ρ_v^c and ρ_v^t for H_2 and other gases at 4880 Å. They find $\rho_v^c=0.0025$ and $\rho_v^t=0.0095$. We calculate, using the thermally averaged (T

$=293^\circ\text{K}$) values of $\alpha(4880 \text{ Å})$ and $\gamma(4880 \text{ Å})$, $\rho_v^c=0.024$ and $\rho_v^t=0.00952$. Bridge and Buckingham² (BB) obtain a formula for ρ_v^c corrected for experimental conditions as

$$\rho_v^c(\omega) = 3\kappa^2(\omega) / 15.3 + 4\kappa^2, \quad (11)$$

where

$$\kappa(\omega) = \gamma(\omega) / 3\alpha(\omega). \quad (12)$$

They find $\rho_v^c=0.0032$, in precise agreement with the value obtained by using our calculated $\alpha(3628 \text{ Å})$ and $\gamma(3628 \text{ Å})$ in Eq. (11). RAB, in suggesting that the BB results for ρ_v^c are too large, have apparently overlooked the fact that the value of $\rho_v^c(6328 \text{ Å})=0.0032$ obtained by BB refers to Eq. (11). The use of the $\gamma(6328 \text{ Å})$ resulting from the measurements of BB in the correct theoretical expression, Eq. (7), gives $\rho_v^c(6328 \text{ Å})=0.0024$ in precise agreement with RAB. We calculate using the theoretical expression of Eq. (7) $\rho_v^c(6328 \text{ Å})=0.00236$ in excellent agreement with both BB and RAB. The excellence of our agreement for ρ_v^t and ρ_v^c with both the BB ($\lambda=6328 \text{ Å}$) and RAB ($\lambda=4880 \text{ Å}$) experiments suggests to us that our computed value for the depolarization ratio for unpolarized light at Lyman- α wavelength is probably quite accurate although rather elaborate wave functions are required to obtain comparable consistency in the $\alpha(\omega)$ at higher frequencies.

An extended version of this manuscript including more extensive tables of polarizability, depolarization ratios, Verdet constants, Rayleigh and Raman scattering cross sections, etc., is being prepared for publication. This manuscript will include a detailed discussion of the process of developing the wave functions used to calculate the oscillator strengths.

This research was supported in part by the Robert A. Welch Foundation of Houston, Texas,

and in part by the National Science Foundation.

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Hyperfine Structures of Optically Inaccessible Excited Atomic States*

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(Received 26 August 1971)

Cascade transitions have been used to produce polarized atoms in optically inaccessible excited states. The polarized fluorescent light which is emitted when the atoms decay can be used to measure hyperfine structures, lifetimes, and other atomic parameters of these inaccessible states. Preliminary measurements of the hyperfine interval for the second excited *S* states of K^{39} , Rb^{85} , Rb^{87} , and Cs^{133} are (in MHz) 46(2), 271(15), 565(40), and 684(50), respectively. To our knowledge, these are the first measurements of excited *S*-state hyperfine intervals in alkali atoms.

The alkalis form a particularly interesting group of atoms since their low-lying energy spectra are due principally to the motion of a single valence electron under the influence of the nucleus and closed shells of inner electrons. However, excitations of the core do have a significant influence on many atomic parameters such as hyperfine coupling constants, fine structure, and oscillator strengths. Thus, the properties of alkali atoms form natural test cases for modern many-body computational techniques. In particular, considerable theoretical work has been done on the hyperfine structure of alkali atoms in the past few years.¹ Precision measurements of hyperfine structures in these atoms are available only for the ground states and the excited *P* states. It would be very interesting to obtain hyperfine-structure measurements for other excited states such as *S* states, *D* states, *F* states, etc. For instance, the low-lying *D*- and *F*-state fine-structure intervals are often inverted. This inversion is believed to be due to core excitations.² Precision hyperfine-structure measure-

ments in these inverted doublets would help to pinpoint the cause of the anomaly. In this Letter we report on a simple new experimental technique which will make it possible to measure the hyperfine structures of many previously inaccessible excited states.

With few exceptions the excited-state hyperfine structure of alkali atoms is smaller than the Doppler width of optical lines. Thus, techniques such as optical double-resonance³ or level-crossing spectroscopy⁴ are necessary for precision measurements, since these methods are limited only by the natural linewidths of the excited states. However, excited *S* states, *D* states, *F* states, etc., have not yet been studied by level-crossing or double-resonance techniques because one cannot excite the states by allowed electric dipole transitions from the ground state. The optically inaccessible states can, however, be excited by electrons, and an electron beam can produce alignment in non-*S* states. Archambault *et al.*⁵ have investigated some of the *D* states in sodium and cesium, but they were only