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Direct-Resolvent-Operator Computations on the Hydrogen-Molecule Dynamic Polarizability, Rayleigh, and Raman Scattering

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Direct sum-over-states methods are used to evaluate the frequency-dependent polarizability and anisotropy for ground-state H_2. Rayleigh and rotational and vibrational Raman cross sections for photon scattering and depolarization ratios are given for Lyman-α radiation. An assessment of the accuracy obtainable by the direct use of sum-over-states methods indicates its high promise as a technique for accurate computation of molecular properties. The Dalgarno–Epstein [J. Chem. Phys. **50**, 2837 (1969)] technique for obtaining a finite-set representation of components of the resolvent operator is shown to be effective for molecules.

I. INTRODUCTION

Perturbation theory can be used to express many properties of atoms and molecules as a sum over matrix elements of complete sets of states of an atomic and molecular system. It has generally been assumed in the past that such a definition of a molecular property was a purely formal statement and could not be reasonably used as a basis for computation. Dalgarno and co-workers,[1] Karplus and Kolker,[2] and Kolker and Michels[3] have shown that the sum-over-states methods can be a very efficient approach for computation of dynamic polarizability of atoms. The work reported here shows that such sum-over-states methods are also a very efficient and accurate means of carrying out computations on molecular systems. (A preliminary report on this work has been given earlier.[4]) This is equivalent to a statement that it is possible to compute a resolvent operator which is effectively complete in some domain of wave-function space. In particular, the use of sum-over-states methods for dynamic polarizability shows that sets of states constructed by a slight modification of ordinary variational procedures can lead to a resolvent-operator expression which is complete in the realm of states reachable by dipole transitions from the ground state.

Dalgarno and Epstein[5] showed that certain sum-over-states formulas (sum rules) are exactly satisfied for properly chosen finite sets of wave functions (which are not necessarily eigenfunctions of the Hamiltonian). It is demonstrated in these computations on the hydrogen molecule that if some finite set of sum rules are forced to be satisfied or very nearly satisfied by the wave functions chosen, then other closely related sum rules will also give very accurate results when carried out over the same set of wave functions.

This technique is being extended to the study of such properties as dipole moments of isotopically different systems (such as HD), magnetic susceptability, nuclear spin-spin interaction, and a variety of properties that can be expressed as sum-over-states formulas. The ability to obtain a high level of accuracy for a set of sum rules will also be expected to have considerable utility in the construction of upper and lower bounds to transition-matrix elements.[6]

The principal results of this study are an accurate set of dynamic polarizabilities and anisotropies for the hydrogen molecule. These quantities can be used to obtain such experimentally interesting quantities as Rayleigh and Raman cross sections and depolarization ratios, Kerr and Verdet constants, index of refraction, and other measures of interaction of radiation with matter. Of particular interest for astrophysics are the values for Lyman-α radiation of the Rayleigh cross section, the ν_{01} Raman cross section, and the depolarization ratio for unpolarized light.

It was also found in the execution of the computations that certain common assumptions such as the use of closure for summing the vibrational and rotational states of molecules are not always justified.

II. SUM RULES, POLARIZABILITY TENSORS, AND DEPOLARIZATION RATIOS

For a diatomic molecule the oscillator strengths in the dipole (length) approximation are defined by the equations

$$f^{\parallel}_{nb} = \tfrac{2}{3}(g_b/g_n)(E_b - E_n)\langle n|z|b\rangle\langle b|z|n\rangle \,, \qquad (1)$$

$$f^{\perp}_{nb} = \tfrac{4}{3}(g_b/g_n)(E_b - E_n)\langle n|x|b\rangle\langle b|x|n\rangle \,, \qquad (2)$$

or the equivalents of (1) and (2) in the dipole velocity

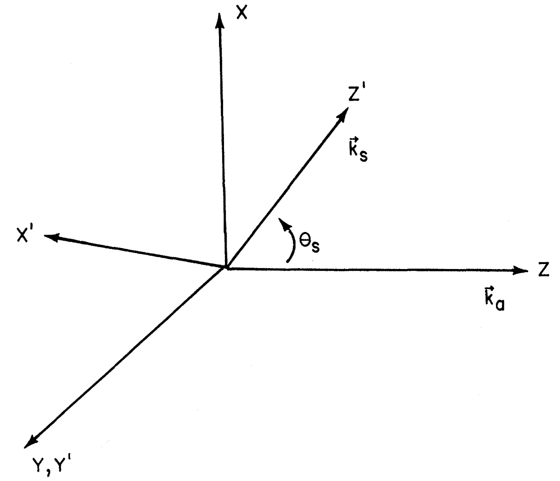

FIG. 1. Definition of the photon scattering angle θ_s. The special case considered here is scattering into the XZ plane of the coordinate system defined by the incident photon.

or acceleration forms of the matrix element. The factors g_n and g_b represent, respectively, the degeneracies of the initial and final rotational levels:

$$f_{nb}=(f^{\parallel}+f^{\perp}). \tag{3}$$

The oscillator strengths can be formed into the familiar set of sum rules:

$$S^{\parallel}(k)=3\textstyle\sum_b f^{\parallel}_{nb}(E_b-E_n)^k , \tag{4}$$

$$S^{\perp}(k)=\tfrac{3}{2}\textstyle\sum_b f^{\perp}_{nb}(E_b-E_n)^k , \tag{5}$$

$$S(k)=\tfrac{1}{3}[S^{\parallel}(k)+2S^{\perp}(k)]. \tag{6}$$

Second-order perturbation theory gives the polarizability of a molecule in response to a photon as

$$\alpha(\omega)=\sum_b\left(\frac{f_{nb}}{(E_b-E_n)^2-\omega^2}\right) . \tag{7}$$

ω is the circular frequency of the photon and atomic units ($\hbar=1$) are assumed. In each of Eqs. (1)–(7) the sum over states extends over all states, electronic, vibrational, and rotational, of the molecule. For a diatomic molecule, the polarizability tensor has two components:

$$\alpha_{\parallel}(\omega)=3\textstyle\sum_b f^{\parallel}_{nb}/[(E_b-E_n)^2-\omega^2] , \tag{8}$$

$$\alpha_{\perp}(\omega)=\tfrac{3}{2}\textstyle\sum_b f^{\perp}_{nb}/[(E_b-E_n)^2-\omega^2] , \tag{9}$$

$$\alpha(\omega)=\tfrac{1}{3}[\alpha_{\parallel}(\omega)+2\alpha_{\perp}(\omega)]. \tag{10}$$

It can be clearly seen that $S(-2)$ is equal to the polarizability for $\omega=0$. The anisotropy of the dynamic polarizability is defined as

$$\gamma(\omega)=\alpha_{\parallel}(\omega)-\alpha_{\perp}(\omega) \tag{11}$$

and $\kappa(\omega)$, a frequently used measure of anisotropy, is given as

$$\kappa(\omega)=\gamma(\omega)/3\alpha(\omega). \tag{12}$$

Experimental values of the polarizability can be obtained via the index of refraction n:

$$n-1=2\pi N\alpha(\omega). \tag{13}$$

N is the number of molecules per unit volume.

The depolarization ratios for the scattered photons are among the experimentally most accessible quantities for photon-scattering experiments. The coordinate system of Fig. 1 has the Z axis in the direction of the incident photons and the Z' axis in the direction of the scattered photons. Define I_{AB} to be the intensity of the beam scattering into an angle θ_s lying in the XZ plane. Assume the polarization of the incident photons is along the Y direction and that the final rotational states are not resolved in the derivation of the intensity formula. Define I^J_{AB} to be identical to I_{AB}, except that rotational states are resolved in the analysis leading to I^J_{AB}. B is the direction of polarization of the incident photon and A the direction of polarization of the scattered photon. Then four depolarization ratios which cover all available experimental data can conveniently be defined:

$$\rho^T_v=\frac{I_{X'Y}}{I_{Y'Y}}\approx\frac{3\gamma^2}{45\alpha^2+4\gamma^2} , \tag{14}$$

$$\rho^T_u=\frac{I_{X'u}}{I_{Y'u}}\approx\frac{6\gamma^2}{45\alpha^2+7\gamma^2}\;\Big|\;\theta_s=90^\circ , \tag{15}$$

$$\rho^c_v=\frac{I^J_{X'Y}}{I^J_{Y'Y}}=\frac{3\gamma^2X_J}{4\gamma^2X_J+45\alpha^2}\approx\frac{\frac{3}{4}\gamma^2}{\gamma^2+45\alpha^2} , \tag{16}$$

$$\rho^c_u=\frac{I^J_{X'u}}{I^J_{Y'u}}=\frac{6\gamma^2X_J}{7\gamma^2X_J+45\alpha^2}\approx\frac{\frac{3}{2}\gamma^2}{\frac{7}{4}\gamma^2+45\alpha^2} , \tag{17}$$

where

$$X_J=\frac{J(J+1)}{(2J-1)(2J+3)} .$$

The subscripts u and v refer, respectively, to unpolarized and vertically polarized (Y axis) incident photons. Clearly ρ^T_v and ρ^T_u include both Rayleigh- and rotational Raman-scattered photons while ρ^c_v and ρ^c_u include only the elastically scattered (Rayleigh) photons. The far-right-hand sides of Eqs. (14)–(17) are the familiar results. The approximation sign appears in (14) and (15) because they are obtained by summing over final rotational levels with neglect of the dependence of scattered-photon frequency and the effect on the final-state vibrational function of the final rotational level. This is a poor approximation for H_2. The approximation sign appears in (16) and (17) because X_J averages to 0.25 in the intensity only as $hcB_e/kT\rightarrow 0$. The depolarization ratios will in many cases, for example, Eq. (15), be functions of scattering angle. Measurements have not been made at angles different from $\theta_s = 90°$ for simple gases, as far as is known to the authors. A number of experiments suggest themselves. For example, $\alpha(\omega)$ could be determined without a knowledge of ρ if measurements are made at $\theta_s = 54° 30'$. It will appear in Sec. V that considerable attention to detail in the derivation of the depolarization ratios is essential if correct comparison to experiment is to be made. Bridge and Buckingham[7] and particularly Chiu[8] and Ford[9] give detailed derivations and analysis of the expressions for I_{AB} and I^J_{AB} and the resulting expressions for the cross sections.

The components of the polarizability tensor also determine the Rayleigh and Raman scattering cross sections. The total cross section for H_2 for a transition $J \rightarrow J'$, $v \rightarrow v'$ is given by[10]

$$Q^{JJ'}_{vv'} = \left(\frac{128\pi^5}{9\lambda'^4}\right)(2J'+1) \times \left[3\alpha^2 \begin{pmatrix} J' & J0 \\ 0 & 00 \end{pmatrix}^2 + \frac{2}{3}\gamma^2 \begin{pmatrix} J' & J2 \\ 0 & 00 \end{pmatrix}^2\right], \tag{18}$$

where λ' is the wavelength of the scattered photon and α and γ are values appropriate to the specific transition. Summing over J', with neglect of dependence of λ' and α, γ on final rotational state, yields the familiar approximate formula

$$Q^T_{vv'} \approx (128\pi^5/9\lambda'^4)(3\alpha^2 + \tfrac{2}{3}\gamma^2). \tag{19}$$

Mean excitation energies $I(k)$ for the passage of fast particles through matter[11] are also given in terms of oscillator strength distributions

$$\ln I(k) = \textstyle\sum_b (E_b - E_n)^k \ln(E_b - E_n) f_{nb}/S(k). \tag{20}$$

$\ln I(-1)$ is related to the cross section for grazing collisions of fast charged particles with atoms or molecules. $\ln I(0)$ is related to the mean energy transference in fast collisions (stopping power). $\ln I(1)$ is related to the mean fluctuation of energy transference in fast collisions and $\ln I(2)$, often called $\ln K_0$, is related to the radiative correction to atomic and molecular energy levels (Lamb shift).

III. WAVE FUNCTION AND CALCULATIONS

The sets of wave functions used in these calculations were chosen to exactly satisfy the sum rules $S(0)$ and $S(-1)$. Such wave functions can be obtained according to the formalism of Dalgarno and Epstein[5] by including in the expansion basis for the wave function such states that Eqs. (21)–(23) are satisfied:

$$\langle\phi_s|H_0|\phi_t\rangle = \mathcal{E}_t\delta_{st}, \tag{21}$$

$$(H_0 - E_0)\psi_0 = 0, \quad \psi_0 \equiv \phi_0 \tag{22}$$

$$V\psi_0 = \textstyle\sum_i a_i\phi_i, \tag{23}$$

where V is a perturbation to H_0. It is easy to obtain a set of wave functions which satisfy these criteria to a high degree of accuracy for the case of $V = \vec{r}$ merely by using the conventional variational configuration-interaction wave-function computation packages. The procedure is to compute a good approximate wave function for the ground state (of, say, n_1 configurations) and good approximate wave functions for the lowest state of symmetries which are reachable from the ground state by dipole transitions (of, say, n_2 configurations). The ground-state wave function is then multiplied by the appropriate component of the $\vec{r}$ vector and added to the wave functions of excited symmetry to give a composite wave function. The Hamiltonian H_0 is then diagonalized in the basis. The resulting set of eigenfunctions then satisfies the sum rules to a high degree of precision. The dipole spectrum of ground state ${}^1\Sigma_g^+$ H_2 includes the ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ states. Several different wave-function sets were tried for the ${}^1\Sigma_g^+$, ${}^1\Sigma_u^+$, and ${}^1\Pi_u$ states to study convergence and obtain a satisfactory representation of the resolvent operator over the full range of internuclear separations. For the ground state of the hydrogen molecule, we used for the first wave function a 14-configuration wave function of ${}^1\Sigma_g$ symmetry which was obtained by full configuration interaction on the orbitals $1s$, $2s$, and $2p$ on both nuclei. The wave function has the form

$$\psi(\vec{r}, R) = \sum_{i=1}^{14} C_i(R)\Phi_i(\vec{r}, R).$$

The $C_i(R)$ are determined variationally and each Φ_i has ${}^1\Sigma_g^+$ symmetry. A contracted notation, e.g., ${}^1\Sigma_g^+(14)$, will be used to refer to the wave functions. The second wave function used for the ground state was a 24-configuration wave function $[{}^1\Sigma_g^+(24)]$ compounded by using full configuration interaction, except for three ionic terms involving the $3d_0$ orbital, on $1s$, $2s$, $2p$, and $3d$ on both nuclei. The orbital exponents for the orbitals were optimized at each internuclear separation. The Dalgarno–Epstein finite-set sum rules are not perfectly satisfied unless ϕ_0 is an exact wave function. We did not find that the sum rules were particularly sensitive to the ground-state wave function so long as wave functions of good quality were used.

For wave functions of ${}^1\Sigma_u$ symmetry, a wave function of 26 configurations $[{}^1\Sigma_u^+(26)]$ constructed without explicit inclusion of the $z\phi_0$ in the expansion basis was used from $R = 1a_0$ to $3a_0$. The orbital exponents were optimized on the lowest state at each internuclear separation. For $R > 3a_0$ and for $0.5a_0 \le R \le 1.0a_0$, a function of 36 configurations, which included a ten-configuration wave function with full configuration interaction on $1s$, $2s$, and $2p$ for the ${}^1\Sigma_u^+$ state plus z times the 14-configuration $X\,{}^1\Sigma_g$ wave function, was used.

$$ {}^1\Sigma_u^+(36) = {}^1\Sigma_u^+(10) + (z)\,{}^1\Sigma_g^+(14) \ . \tag{24} $$

A 52-term wave function constructed by

$$ {}^1\Sigma_u^+(52) = {}^1\Sigma_u^+(26) + (z)\,{}^1\Sigma_g^+(14) \tag{25} $$

was used to test convergence.

For the states of ${}^1\Pi_u$ symmetry, two wave functions were used. A 28-configuration wave function $[{}^1\Pi_u(28)]$ was compounded by taking six terms, full configuration interaction on 1*s*, 2*s*, and 2*p* with orbital exponents optimized on the lowest state at each internuclear separation, to which was added the 14-configuration ground-state wave function multiplied by $(x+iy)$:

$$ {}^1\Pi_u(28) = {}^1\Pi_u(6) + (x+iy)\,{}^1\Sigma_g^+(14) \ . \tag{26} $$

The second wave function used for the ${}^1\Pi_u$ states to check for convergence was a 40-configuration wave function compounded according to the equation

$$ {}^1\Pi_u(40) = {}^1\Pi_u(18) + (x+iy)\,{}^1\Sigma_g^+(14) \ . \tag{27} $$

${}^1\Pi_u(18)$ is a wave function with orbital basis 1*s*, 2*s*, 2*p*, and 3*d* on each nuclei and full orbital exponent optimization on the lowest state. The wave function contained all covalent configurations that result from full configuration interaction on the basis; only the three ionic configurations $(1s2p+)$, $(1s3d+)$, and $(1s3p+)$ are included. The transitional-matrix elements with the larger ${}^1\Pi_u$ and ${}^1\Sigma_u^+$ wave functions were computed using the 24-configuration ${}^1\Sigma_g^+$ function. Comparable levels of accuracy in the wave functions seem to be essential, so that the error in the transition energy will be minimized.

The sets of wave functions were grouped into two sets for the computation of the $f_{nb}^{\parallel}$ and $f_{nb}^{\perp}$ distributions, which are the basic data for the computation of $\alpha(\omega)$, $\gamma(\omega)$, etc. Set 1 computes $f_{nb}^{\parallel}$ from ${}^1\Sigma_g^+(14)$ and ${}^1\Sigma_u^+(26)$ for $1.0a_0 \leq R \leq 3.0a_0$, ${}^1\Sigma_g^+(14)$ and ${}^1\Sigma_u^+(36)$ for $0.5a_0 \leq R < 1.0a_0$ and for $3.0a_0 < R \leq 8.0a_0$, and $f_{nb}^{\perp}$ from ${}^1\Sigma_g^+(14)$ and ${}^1\Pi_u(28)$ for $0.5a_0 \leq R \leq 8.0a_0$. Set 2 computes $f_{nb}^{\parallel}$ from ${}^1\Sigma_g^+(24)$ and ${}^1\Sigma_u^+(52)$ for $1.0a_0 \leq R < 3.0a_0$.

IV. SUM-RULE COMPUTATIONS FOR H_2 FOR STATIC QUANTITIES

We report in this section some results obtained using sum-rule functions as defined in Eqs. (28)–(33):

$$ S(-2) = \alpha(0) \ , \tag{28} $$

$$ S(-1) = \tfrac{2}{3}\langle n|\vec{\mathrm{r}}\cdot\vec{\mathrm{r}}\,|n\rangle \ , \tag{29} $$

$$ S(0) = N \equiv \text{the number of electrons,} \tag{30} $$

$$ S(1) = -\tfrac{2}{3}\langle n|\Big(\sum_{j=1}^{N}\vec{\mathrm{P}}\Big)^2\,|\,n\rangle \ , \tag{31} $$

$$ S(2) = -\tfrac{4}{3}\pi\textstyle\sum_a Z_a\langle n|\displaystyle\sum_{j=1}^{N}\delta(r_{ja})|n\rangle \tag{32} $$

$$ = -\tfrac{1}{3}\langle n|\nabla^2 V|n\rangle \ . \tag{33} $$

In (33), *V* is the total potential-energy operator of the system. Each sum-rule function can be decomposed into parallel ($\parallel$) and perpendicular ($\perp$) components. These are all static quantities. The principal quantities of this paper are those related to frequency-dependent polarizability, e.g., Rayleigh and Raman scattering cross sections, depolarization ratios, etc. Nonetheless, the accuracy obtainable with sum-over-states methods for a spectrum of sum rules for the static quantities would seem to be of interest when considering extensions of this technique to other static properties. It should be observed that the sum rules $S(-1)$ and $S(0)$ should be exactly satisfied by the wave functions used in these computations provided that the ground-state wave function is an exact wave function and that the diagonalizations are carried out to exact accuracy. Additionally, the length and velocity forms to the matrix elements should be identical under the same conditions.[5] It will be seen that $S(-2)$ is also very accurately satisfied for the static case. However, the sum rules of higher index, $S(1)$ and $S(2)$, are not so accurately obtained. Table I contains the expectation values of the sum rules for a single internuclear separation together with accurate results where they are available and diagonal expectation values where this is practical. Table II contains rotation-vibration averages of the static polarizability tensor for several *J* values and for a single *J* value for the $0 \rightarrow 1$ vibrational transition.

Examining these results corroborates clearly that the sum rules $S(-2)$ to $S(0)$ are very accurately satisfied. The sum rules that weight the continuum portion of the oscillator strength, $S(1)$ and $S(2)$, appear to be less accurate.

A particularly interesting comparison for the states polarizabilities is the quantity $\kappa(0)$. Nelissen, Reuss, and Dymanus[12] directly measure $\kappa(0)$ by a beam-deflection measurement in static electric and magnetic fields. They find $\kappa = 0.112 \neq 0.002$. This is in considerable disagreement with the value of $\kappa(6328\ \text{Å}) = 0.128 \pm 0.002$ found by Bridge and Buckingham from photon scattering and

TABLE I. Sum rules for $R = 1.4a_0$.

k	$S''(k)$	$\langle n\vert\bar{0}\vert n\rangle^{a}$	$\langle n\vert\bar{0}\vert n\rangle^{b}$	$S^{\perp}(k)$	$\langle n\vert\bar{0}\vert n\rangle^{a}$	$\langle n\vert\bar{0}\vert n\rangle^{b}$
−2	6.3517		6.3805	4.5693		4.5777
−1	3.4452	3.4590	3.4534	2.8248	2.7894	2.8264
+0	1.9885		2.0	2.0041		2.0
+1[c]	1.6365	1.7066	1.7012			
+2[c]	1.9992	3.8636	3.8550			

[a] Computed from the 24-term ${}^1\Sigma_g^+$ wave function.

[b] W. Kolos and L. Wolniewicz, J. Chem. Phys. 41, 3663 (1964).

[c] The results here are for $S(k) = \frac{1}{3}(S^{\parallel} + 2S^{\perp})$.

TABLE II. Vibration-rotation averages of the static polarizability tensor.

$v=0$ vibrational level	$\alpha_{00}^{JJ}=\frac{1}{3}(2\alpha_\perp+\alpha_\parallel)$		$\gamma_{00}^{JJ}=\alpha_\parallel-\alpha_\perp$	
	This work[a]	KW results[b]	This work[a]	KW results[b]
$J=0$	$5.3981a_0^3$	$5.4139a_0^3$	$2.0060a_0^3$	$2.0239a_0^3$
1	5.4090	5.4235	2.0138	2.0317
2	5.4284	5.4427	2.0289	2.0474
3	5.4573	5.4714	2.0515	2.0709
4	5.4957	5.4292	2.0818	2.1022
thermal average over rotational levels for $T=300\,°\mathrm{K}$	5.4144	5.4292	2.0182	2.0360
Nondiagonal matrix elements ($J=J'=0,\ v=0,\ v'=1$)	α_{01}^{00}		γ_{01}^{00}	
	This work[c]	KW results[b]	This work[c]	KW results[b]
	$0.7401a_0^3$	$0.7380a_0^3$	$0.6080a_0^3$	$0.6097a_0^3$

[a] f_{nb} computed from set-1 wave functions (see text). The f_{nb} from set-2 wave functions yields $\alpha_{00}^{00}=5.411a_0^3$ and $\gamma_{00}^{00}=2.029a_0^3$.

[b] W. Kolos and L. Wolniewicz, J. Chem. Phys. 51, 5002 (1969).

[c] f_{nb} computed from set-2 wave functions (see text). The f_{nb} from set-1 wave functions yields $\alpha_{01}^{00}=0.7326a_0^3$ and $\gamma_{01}^{00}=0.5857a_0^3$.

with the value of $\kappa(0)=0.125$ computed by Kolos and Wolniewicz. The value computed in this study is $\kappa(0)=0.126$. MacAdam and Ramsey[13] have measured $\gamma(0)$ by a beam-magnetic-resonance method and find $\gamma(0)=2.035\pm0.003a_0$. Using the Kolos-Wolniewicz value for $\alpha(0)$ in Eq. (12), $H(0)=0.125$ is obtained. It would appear that Nelissen, Reuss, and Dymanus have an undetected error in their experiment or interpretation of the experiment.

Tables III and IV show the convergence of computed $S(1)$ and $S(2)$ with respect to wave-function size. $S(1)$ appears to have become very stable with respect to wave-function size, whereas $S(2)$ is clearly unstable as yet, which indicates deficiency in the continuum representation. Our procedures apparently yield a poor description of the high-energy portion of the oscillator strength distribution for the ${}^1\Pi_u$ states. The set of states of Π symmetry that lie high in the continuum and correspond approximately to doubly excited electronic states of H_2 have appreciable oscillator strength. The spectrum of the ${}^1\Sigma_u^+$ states has very little oscillator strength in the electronic continuum.

TABLE III. Convergence of computed $S(1)$ with respect to wave-function size.

	$S^\parallel(1)$		
R	$X(14)$; ${}^1\Sigma_u^+(26)$	$X(14)$; ${}^1\Sigma_u^+(36)$	$X(24)$; ${}^1\Sigma_u^+(62)$
1.0	1.6915	1.7632	1.7779
1.4	1.2655	1.3782	1.3789
3.0	0.9335	1.0061	1.0056
	$S^\perp(1)$		
R		$X(14)$; ${}^1\Pi_u(28)$	$X(24)$; ${}^1\Pi_u(40)$
1.4		1.7653	1.7678
2.0		1.4371	1.4761

TABLE IV. Convergence of computed $S(2)$ with respect to wave-function size.

	$S^\parallel(2)$		
R	$X(14)$; ${}^1\Sigma_u^+(26)$	$X(14)$; ${}^1\Sigma_u^+(36)$	$X(24)$; ${}^1\Sigma_u^+(52)$
1.0	3.6450	5.2048	5.7148
1.4	1.9320	3.8056	4.0106
3.0	1.7304	2.0966	2.2162
	$S^\perp(2)$		
R		$X(14)$; ${}^1\Pi_u(28)$	$X(24)$; ${}^1\Pi_u(40)$
1.4		3.9922	4.0246
2.0		2.5820	2.9442

Table V contains the expectation values for mean excitation energies as computed from our sum-rule values. It would be anticipated from our other results that our $I(-1)$ and $I(0)$ should be very

TABLE V. Values of mean excitation energy functions $\ln I(k)=\sum_b(E_b-E_n)^k\ln(E_b-E_n)f_{nb}/S(k)$.

$I(\tau)$ from the expectation value of $\ln I(\tau)$ for the $v=0$ vibrational level, thermal average over rotational levels				
	$I(-1)$	$I(0)$	$I(1)$	$I(2)$
This work[a]	16.43 eV	19.21 eV	25.39 eV	44.66 eV
Previous values	16.28[h]	18.6[b] 19.5 ± 0.5[d] 18.3 ± 2.6[e] 18.7[h]	31.8[h]	61.66[c] 247.2[d] 269.3[f]
$R=1.4$ fixed nuclei value for $I(0)$				
This work				19.52 eV
Kamikawai *et al.*[g]				18.2 eV

[a] f_{nb} computed from set-2 wave functions (see text).

[b] Reference 20.

[c] Lower bound, L. Wolniewicz, J. Chem. Phys. 45, 515 (1966).

[d] J. D. Garcia, Phys. Rev. 147, 66 (1966).

[e] Experimental value, F. W. Martin and L. C. Northcliffe, Phys. Rev. 128, 1166 (1962).

[f] Hydrogen-atom exact value, H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1957), Vol. 35/1.

[g] R. Kamikawai, T. Watanabe, and A. Amemiya, Phys. Rev. 184, 303 (1969).

[h] P. W. Langhoff and A. C. Yates, J. Phys. B 5, 1071 (1972).

accurate.

It was noted in the computations that the exact equality between length and velocity forms of the matrix element which would in principle result from the exact application of the Dalgarno–Epstein finite-sum-rule procedure was not obtained. It was consistently found that use of an average of the length and velocity matrix elements was more accurate than either separately. This is in accord with the results of Hansen[14] and others.

V. RESULTS FOR H_2 DYNAMIC QUANTITIES

The principal quantities of interest are $\alpha(\omega)$ and $\gamma(\omega)$. Equations (14)–(19) show that nearly all quantities of interest for photon scattering can be obtained if $\alpha(\omega)$ and $\gamma(\omega)$ are known over the complete range of internuclear separations. Table VI contains α and γ at a fixed internuclear separation of $R=1.4a_0$ (a_0 is the Bohr radius) together with comparisons with previous computations. The agreement between the best of these previous computations, Langhoff and Karplus[15] and Epstein,[16] is seen to be excellent. Table VII has the vibrationally and rotationally averaged ($T=293$ °K) dynamic polarizabilities and anisotropies as a function of frequency from Lyman-α to infinite wavelength. No previous computations of dynamic polarizabilities have been carried out with vibrational averaging over initial- and final-state vibrational functions. These are compared with semiempirical results of Dalgarno and Victor[17] and the experimental results (also as compiled by Dalgarno and Victor). Table VIII reports the same quantities for the $0\rightarrow 1$ Raman vibrational transition averaged at 300 °K. Extensive tables of $\alpha(\omega)$ and $\gamma(\omega)$ for sets of allowed rotation levels for Rayleigh and Raman scattering are available on request.[9]

The use of closure to sum over the vibrational levels of the intermediate states becomes successively less accurate as the wavelength of the incident photon becomes shorter. It was found necessary to introduce explicit summation over the vibration levels and integration over the nuclear translation continuum for the $C\,^1\Pi_u$ and $B\,^1\Sigma_u^+$ states. The effect of closure was very marked for the $0\rightarrow 1$ vibrational excitation matrix element. Explicit summation and integration produced, for example, a 6.8% correction for $\alpha''_{00}(1215.7)$ but a 42% correction for $\alpha''_{01}(1215.7)$. A thorough analysis of the deficiencies of closure is given by Ford.[9]

TABLE VI. Comparison of computed $\alpha(\omega)$ and $\gamma(\omega)$ values to previous computations at $R=1.4a_0$.

Wavelength (Å)	Present work	IRE[a]	LK[b]	HPK[c]		KWA[d]	VBD[e]	AE[f]
			$\alpha(\omega)$ (a_0^3)					
∞	5.18	5.21	5.23	5.20	(5.37)	5.43	5.23	5.406
6328.0	5.28	5.31	5.32	5.29	(5.47)	5.52	5.31	5.50
5462.3	5.31	5.34	5.36	5.32	(5.50)	5.55	5.35	5.53
4359.6	5.39	5.42	5.43	5.39	(5.58)	5.63	5.42	5.60
4047.7	5.42	5.46	5.47	5.43	(5.62)	5.66	5.45	5.64
2968.0	5.65	5.68	5.70	5.63	(5.86)	5.88	5.65	5.85
2302.9	6.01	6.03	6.07	5.96	(6.23)	6.24	5.98	6.19
1854.6	6.59	6.60	6.67	6.50	(6.85)	6.80	6.49	6.73
1600.0	7.31	7.29	7.40	7.12	(7.66)	7.48	7.08	7.36
1400.0	8.44	8.36	(8.58)	8.21	(8.71)	8.44	8.05	8.30
1215.7	11.02	10.40	(11.17)	10.05	(12.30)	10.68		10.12
			$\gamma(\omega)$ (a_0^3)					
∞	1.84	1.84	1.83	1.95		1.64	1.67	1.65
6328.0	1.90	1.86	1.88	2.00		1.68	1.74	1.69
5462.3	1.92		1.90	2.02		1.69	1.75	1.71
4359.6	1.96		1.94	2.07		1.73	1.78	1.74
4047.7	1.98		1.96	2.09		1.75	1.79	1.76
2968.0	2.11		2.09	2.23		1.86	1.90	1.86
2302.9	2.32		2.30	2.46		2.05	2.08	2.04
1854.6	2.69		2.66	2.86		2.36	2.39	2.32
1600.0	3.16		3.13	3.31		2.77	2.74	2.67
1400.0	3.95		(3.93)	4.42		3.36	3.42	3.23
1215.7	6.12		(5.92)	5.78		5.07	4.50	4.45

[a] Reference 13.

[b] Reference 12.

[c] H. P. Kelly, Phys. Rev. A 1, 274 (1970). The values of $\alpha(\omega)$ in parentheses are calculated by shifting the 1s orbital energy by an amount chosen so that the results are in better agreement with experiment.

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TABLE VII. Comparison of $\alpha(\omega)$ and $\gamma(\omega)$ to semiempirical calculations and to experiment.

Wavelength (Å)	This work[a]	Semi-empirical[b]	Expt.[b]	% diff. (this work vs expt.)
		$\alpha(\omega)$ (a_0^3)		
∞	5.406	5.450	5.437	0.6%
6943.0	5.492			
6328.0	5.509	5.554	5.554	0.8
5462.3	5.545	5.591	5.582	0.7
4880.0	5.581			
4359.6	5.628	5.675	5.667	0.7
4079.0	5.662	5.708	5.701	0.7
4047.7	5.666	5.713	5.705	0.8
3342.4	5.797	5.845	5.840	0.7
2968.1	5.913	5.963	5.960	0.8
2753.6	6.006	6.056	6.055	0.8
2535.6	6.130	6.182	6.183	0.9
2379.1	6.246	6.299	6.303	0.9
2302.9	6.313	6.368	6.384	1.1
1990.5	6.707	6.766	6.771	1.0
1935.8	6.804	6.865	6.868	0.9
1862.7	6.954	7.017	7.017	0.9
1854.6	6.973	7.035	7.035	0.9
1700.0	7.402	7.471		
1600.0	7.797	7.872		
1500.0	8.348	8.431		
1400.0	9.165	9.262		
1300.0	10.509	10.625		
1215.7	12.603	12.765	12.2[c]	3.2
		$\gamma(\omega)$ (a_0^3)		
∞	2.005	2.029		
6943.0	2.056			
6328.0	2.066	2.092	2.09[d,e]	1.0
5462.3	2.087	2.115		
4880.0	2.109			
4359.6	2.137	2.168		
4079.0	2.157	2.188		
4047.7	2.160	2.191		
3342.4	2.240	2.274		
2968.1	2.312	2.350		
2753.6	2.370	2.410		
2535.6	2.450	2.492		
2379.1	2.524	2.569		
2302.9	2.569	2.615		
1990.5	2.834	2.889		
1935.8	2.901	2.958		
1862.7	3.007	3.067		
1854.6	3.020	3.080		
1700.0	3.333	3.401		
1600.0	3.635	3.710		
1500.0	4.077	4.159		
1400.0	4.783	4.871		
1300.0	6.074	6.158		
1215.7	8.428	8.495		

Coefficients in the Cauchy expansion of $\alpha(\omega)$

$$\alpha(\omega)=\sum_{k=0}^{\infty}\alpha_k(\omega^2)^k$$

TABLE VII. (*Continued*)

	α_k	
k	This work[a,f]	From experimental refractive index data[g]
0	5.379	5.439
1	19.35	20.02
2	78.60	81.62
3	343.00	350.00

[a] f_{nb} computed from wave function set 1 (see text). The $\alpha(\omega)$ reported is a thermal average ($T = 293$ °K) over rotational levels. Explicit summation of vibrational levels of the $B\,^1\Sigma_u^+$ and $C\,^1\pi_u$ states was carried out.

[b] Reference 20.

[c] Reference 21.

[d] From the experimentally determined molecular anisotropy values, $\kappa(\omega)=\gamma(\omega)/3\alpha(\omega)$ using our calculated $\alpha(\omega)$.

[e] Reference 7.

[f] Integration over nuclear continuum for $B\,^1\Sigma_u^+$ and $C\,^1\Pi_u$ not included in these computations.

[g] Reference 12.

The accuracy of the dynamic polarizability as a function of frequency requires little comment with the exception of Lyman-α. The results are generally in agreement with experiment to approximately 1%. An accurate experimental value of the anisotropy is available at only a single frequency. The agreement with this one experimental point is very good, within 1%. The discrepancy at Lyman-α has some question concerning it. This measurement was taken by Gill and Heddle[18] and depends directly upon the value of the depolarization ratio since their measurement is of the quantity $(n-1)\times(6+6\rho)/(6-7\rho)$. The value of $\alpha(1215.7)$ listed here was extracted from their measurement using our computed value of $\rho_u^T = 0.0558$ for Lyman-α. Gill and Heddle normalized their results to an older value of ρ_u^T for N_2. Nonetheless later experiments appear to confirm the accuracy of the Gill–Heddle result.[19] Comparisons to semiempirical and experimental work for α_{01} and γ_{01} are available at Lyman-α and at 4047 Å. Dalgarno and Williams[10] find these quantities to be $\alpha_{01}(1215.7\ \text{Å}) = 2.31a_0^3$ and $\gamma(1215.7\ \text{Å}) = 3.52a_0^3$. Results found in this study are $3.81a_0^3$ and $4.977a_0^3$. The experimental result for α_{01} and the ratio between anisotropy and the polarizability at 4047 Å are obtained from the work of Golden and Crawford[10] and Yoshino and Bernstein.[11] These authors find, respectively, $\alpha_{01}(4047\ \text{Å}) = 0.770 \pm 0.062a_0^3$ and $0.73a_0^3$. The computed result given here is $0.801a_0^3$, which is well within the experimental limits set by Golden and Crawford. The computed values for the ratio $\alpha_{01}(4047\ \text{Å})/\gamma_{01}(4047\ \text{Å})$ are within experimental error. Golden and Crawford find this ratio equal to 0.775 ± 0.171, while Bernstein and Yoshino find 0.76. The computed value in this work is 0.841.

TABLE VIII. $\alpha_{01}^{JJ}(\omega)$ and $\gamma_{01}^{JJ}(\omega)$ thermal average over rotational levels ($T = 300$ °K).[a]

Wavelength (Å)	$\alpha_{01}(\omega)$ (a_0^3)	$\gamma_{01}(\omega)$ (a_0^3)
∞	0.740	0.613
6328.0	0.761	0.634
5462.3	0.770	0.643
4359.6	0.791	0.663
4079.0	0.800	0.672
4047.7	0.801	0.674
3342.4	0.835	0.709
2968.1	0.866	0.742
2753.6	0.892	0.769
2535.6	0.927	0.806
2379.1	0.960	0.841
2302.9	0.980	0.864
1990.5	1.098	0.990
1935.8	1.130	1.029
1862.7	1.178	1.084
1854.6	1.184	1.091
1700.0	1.328	1.261
1600.0	1.468	1.432
1500.0	1.676	1.696
1400.0	2.013	2.146
1300.0	2.640	3.057
1215.7	3.810	4.977
1150.0	6.348	9.974

Comparison to previous values

Semiempirical[b]	This work
$\alpha_{01}(1215.7\ \text{Å}) = 2.31a_0^3$	$3.810a_0^3$
$\gamma_{01}(1215.7\ \text{Å}) = 3.52a_0^3$	$4.977a_0^3$
Expt.	
$\alpha_{01}(4047\ \text{Å}) = 0.770 \pm 0.062a_0^3$[c]	$0.801a_0^3$
$= 0.730a_0^3$[d]	
γ_{01}/α_{01} (4047 Å) $= 0.775 \pm 0.171$[c]	0.841
$= 0.76$[d]	

[a] f_{nb} computed from wave function set 2 (see text).
[b] Reference 17.
[c] Reference 18.
[d] Reference 19.

The depolarization ratios are perhaps the most interesting and sensitive experimental results that can be obtained for Rayleigh and Raman scattering. Table IX gives the ρ_v^c and ρ_v^T ratios for 4880 Å computed in this work as a function of J. The accurate rather than approximate forms of Eqs. (14) and (16) were used, as described below. Rowell, Aval, and Barrett (RAB)[22] measure ρ_v^c as 0.0025 and measure $\rho_v^T = 0.0095$. These values were then "verified" through the use of the relation

$$\rho_v^c = (\tfrac{1}{4}\rho_v^T)/(1 - \rho_c^T).$$

Since the forms quoted by RAB for ρ_v^c and ρ_v^T are only approximately valid for H_2, the verification is fortuitious. In Paper I, where the right-hand sides of Eqs. (14) and (16) were used to compute values of ρ_v^c and ρ_v^T to compare with RAB, excellent agreement was obtained. The thermally averaged value for ρ_v^c, obtained with the more correct middle form of Eq. (16), yields $\rho_v^c = 0.00306$. A computation of ρ_v^T from the definition of $I_{X',Y}^J / I_{Y',Y}^J$ with $I_{X',Y}^J$ and $I_{Y',Y}^J$ summed over the Q, 0, and S branches and thermally averaged ($T = 293$ °K) yields ρ_v^T

TABLE IX. Depolarization ratios as a function of rotation states.

J	ρ_v^c (4880 Å)	ρ_v^T (4880 Å)
0	0.0	0.00869
1	0.00378	0.00873
2	0.00272	0.00884
3	0.00258	0.00890
4	0.00256	

TABLE X. Dispersion-force coefficients for a pair of hydrogen molecules.

$R = 1.4$ fixed nuclei values		
	Present work[a]	LGK[b]
C	11.35	11.5
Γ	0.0985	0.097
Δ	0.0102	0.010
Values for $v = 0$ vibrational level		
	Present work[a,c]	VD[d]
C	12.09	12.4
Γ	0.1031	0.101
Δ	0.0112	0.011

[a] f_{nb} computed from set-1 wave functions (see text).
[b] P. W. Langhoff, R. G. Gordon, and M. Karplus, J. Chem. Phys. 55, 2126 (1971).
[c] For $J = 1$ rotational level.
[d] G. A. Victor and A. Dalgarno, J. Chem. Phys. 53, 1316 (1970).

TABLE XI. Results for Lyman-α radiation. Thermal average over rotational and vibrational states at 300 °K. The exact rather than approximate formulas are used for the depolarization ratios and cross sections. Only at this wavelength are the approximate formulas for $\rho_{v,u}^c$ in error.

$\alpha_{00} = 12.538a_0^3$, $\gamma_{00} = 8.342a_0^3$
$\alpha_{01} = 3.810a_0^3$, $\gamma_{01} = 4.977a_0^3$
$\rho_v^c = 0.00745$, $\rho_u = 0.0147$ ($\theta_s = 90°$)
$\rho_v^T = 0.0287$, $\rho_u^T = 0.0558$
$Q_{00}^c = 2.129 \times 10^{-24}\ \text{cm}^2$
$Q_{00}^T = 2.265 \times 10^{-24}\ \text{cm}^2$
$Q_{01}^T = 2.146 \times 10^{-25}\ \text{cm}^2$

$= 0.00875$. The agreement reported in Paper I with the experimental work of Bridge and Buckingham persists, the most direct comparison being the anisotropy at 6328 Å which is in agreement to within 1%. We conclude that the failure of RAB to consider the breakdown for H_2 of the assumptions leading to the far right-hand sides of Eqs. (14)–(17) render a reanalysis of their results for H_2 of interest. It must be noted that Bridge and Buckingham have derived formulas equivalent to those used in this analysis.

Dispersion-force coefficients for pairs of hydrogen molecules can also be obtained from this work. Table X contains values at a fixed internuclear separation and also vibrationally averaged values. These are compared to the only previous computations and to semi-empirical work by Victor and Dalgarno. The agreement can be seen to be quite good.

VI. CONCLUSION

It has been demonstrated in this paper that sum-over-states methods can be applied directly to variationally obtained wave functions to obtain very accurate results for frequency-dependent quantities such as polarizability, anisotropy, Rayleigh and Raman scattering, etc. This implies directly that it is possible to compute resolvent operators that are complete in domains of interest. This work is being extended to consider other operators, such as nuclear spin-spin interactions, magnetic susceptabilities, dipole shielding constants, etc. It is hoped that the Rayleigh and Raman cross sections listed here for Lyman-α radiation are of interest to astrophysicists for the study of radiation passing through outer space and in particular for the determination of the densities of molecular hydrogen and HD in interstellar clouds and stars. The results for Lyman α are collected, for convenience, in Table XI.

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