The above implies

$$\int V_c^m(\vec{r})\,d\vec{r}=0 \quad . \tag{10b}$$

This, however, contradicts the fact that $V_c^m(r)$ is non-negative. We then conclude that the factorization of the correlation function in the form given by (8) is unlikely to give a valid representation of its nonlocality.

In contrast as already indicated, our derivation of (7) does not involve a separable approximation for the correlation function, and the validity of the resulting pair of coupled equations does not depend on the separability of the correlation function. The coupling potential V_c given by (7b) is obtained by solving the inverse problem corresponding to the phase-shift matrix (3), and it differs from the one given by (8). Equations (7) are to be viewed as replacing the second-order optical potential by a pair of coupled local Schrödinger equations, and insofar as elastic scattering is concerned the separability of the correlation function is a sufficient but not necessary condition for their equivalence.

In conclusion, we have shown that the small-angle limitation due to the use of the eikonal approximation may be removed without involving a separable approximation for the correlation function, and the second-order optical potential is essentially equivalent to solving a system of two coupled local Schrödinger equations with coupling potentials which are related to the correlation function through an Abel integral equation. We wish to stress that the above conclusion specifically refers to the second-order optical potential, which as already indicated depends only on the one- and two-body densities. Including higher-order terms in the optical potential would lead to a different system of equations than (8), and this deserves further research. The above results are quite general, and they may, if conditions are appropriate, be equally well applied to any elastic scattering by a many-body system.

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Molecular Parameters of the O_2 Molecule

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By analyzing all existing frequency data of the oxygen molecule in microwave, submillimeter, and infrared spectroscopy, a new set of values for molecular parameters is obtained. Our values are $B_0=43.100518$, $B_1=-1.44962\times10^{-4}$, $B_2=-1.57\times10^{-10}$, $\lambda_0=59.501342$, $\lambda_1=5.847\times10^{-5}$, $\mu_0=-0.252586$, and $\mu_1=-2.464\times10^{-7}$ in GHz.

I. INTRODUCTION

Since the electronic ground state of the $O^{16}O^{16}$ molecule is ${}^3\Sigma_g^-$, each rotational level is a triplet. Theory of this fine structure is given by Kramers,[1] Hebb,[2] and Schlapp.[3] Many experiments have been performed in microwave spectroscopy[4] to measure the energy separations within each triplet, but Zimmerer and Mizushima[5] and West and Mizushima[6] remeasured most of these lines with an accuracy of two parts in 10^7.

A refined theory including the effect of centrifugal stretching was developed by Mizushima and Hill[7] and applied to accurate microwave data.[5,6] However, there was an arithmetic error in West and Mizushima's paper,[6] and the values of molecular parameters they proposed were incorrect. Tischer[8] and Wilheit and Barrett[9] corrected the mistake and proposed revised sets of values for the molecular parameters.

Recently Waters[10] measured one more microwave line, McKnight and Gordy[11] measured $N=1\rightarrow 3$ transitions in submillimeter wave spectroscopy, and Evenson and Mizushima[12] measured $N=13\rightarrow 15$ and $N=21\rightarrow 23$ transitions using a new technique of laser magnetic resonance (LMR). In view of these new data we have determined a new set of molecular parameters in this paper incorporating both old and new data.

II. THEORY

After making the Born-Oppenheimer approximation, the effective Hamiltonian for nuclear motion is

$$\hat{H}=\hat{H}_{\mathrm{vib}}+\hat{H}_{\mathrm{rot}} , \tag{1}$$

where $\hat{H}_{\mathrm{vib}}$ contains the vibrational kinetic energy and the adiabatic potential. The rotational Hamiltonian is

$$H_{\mathrm{rot}}=\hat{B}\hat{N}^2+\tfrac{2}{3}\hat{\lambda}(3\hat{S}_z^2-\hat{S}^2)+\hat{\mu}\hat{N}\cdot\hat{S} , \tag{2}$$

where the first term is the rotational kinetic energy and the others are the Kramers and Schlapp coupling terms.[1,3] Suppose we know the eigenvalues and eigenfunctions of H_{vib}:

$$\hat{H}_{\mathrm{vib}}\,|\,v\rangle=E_v\,|\,v\rangle , \tag{3}$$

then multiplying $|v\rangle$ by $|NSJM\rangle$, which are the eigenfunctions of $\hat{N}^2$, $\hat{S}^2$, $\hat{J}^2$, and $\hat{J}_z$, we obtain the basis functions which are used to construct the matrix of $\hat{H}$. The resulting matrix is almost diagonal except for nondiagonal matrix elements of $\hat{H}_{\mathrm{rot}}$ between different vibrational states and the matrix elements of the Kramers term between N states and $(N\pm 2)$ states.

The effect of $\hat{H}_{\mathrm{rot}}$ can be treated by means of degenerate perturbation theory. It has been shown[13] that an answer correct to the third order of H_{rot} can be obtained by first treating all excited vibrational states in terms of a space contraction operator, and then diagonalizing the matrix for each rotational state. This procedure is the same as the one we took before[5-7] and equivalent to the method taken by Wilheit and Barrett.[9] Thus, the paper by Mizushima[13] guarantees that existing formulas are correct to the third order if we take

$$\begin{aligned}
&\langle 0|\hat{B}|0\rangle=B_0,\quad \sum_{v\neq 0}|\langle 0|\hat{B}|v\rangle|^2(E_0-E_v)^{-1}=B_1 ,\\
&\sum_{\substack{v\neq 0\\ v'\neq 0}}\langle 0|\hat{B}|v\rangle\langle v|\hat{B}|v'\rangle\langle v'|\hat{B}|0\rangle[(E_0-E_v)(E_0-E_{v'})]^{-1}-B_0\sum_{v\neq 0}|\langle 0|\hat{B}|v\rangle|^2(E_0-E_v)^{-2}=B_2 ,\\
&\langle 0|\hat{\lambda}|0\rangle=\lambda_0,\quad \sum_{v\neq 0}2\langle 0|\hat{\lambda}|v\rangle\langle v|\hat{B}|0\rangle(E_0-E_v)^{-1}=\lambda_1 ,\\
&\langle 0|\hat{\mu}|0\rangle=\mu_0,\quad \sum_{v\neq 0}2\langle 0|\hat{\mu}_B|v\rangle\langle v|\hat{B}|0\rangle(E_0-E_v)^{-1}=\mu_1 .
\end{aligned} \tag{4}$$

In each of the resulting triplets it is known that the highest state is an eigenstate of $\hat{N}^2$ and $\hat{J}^2$ such that $N=J$, but the other two states are not eigenstates of N^2. In order to express energies of these states, it is convenient to introduce an effective "quantum number" n such that $n=N$ in the highest state and that $N\rightarrow n$ in the limit of $\lambda/B\rightarrow 0$ in the other two states. Then we have the following:

$$E(J=N=n)=B_0n(n+1)+B_1n^2(n+1)^2+B_2n^3(n+1)^3+\tfrac{2}{3}\lambda_0+\tfrac{2}{3}\lambda_1n(n+1)-\mu_0-\mu_1n(n+1) , \tag{5a}$$

$$\begin{aligned}
E(J=n-1)={}&B_0(n^2-n+1)+B_1(n^4-2n^3+7n^2-6n+2)+B_2(n^6-3n^5+18n^4-31n^3+33n^2-18n+4)\\
&-\tfrac{1}{3}\lambda_0-\tfrac{1}{3}\lambda_1(n^2-n+4)-\tfrac{1}{2}\mu_1(7n^2-7n+4)+\{[B_0(2n-1)+B_1(4n^3-5n^2+4n-1)\\
&+B_2(6n^5-15n^4+32n^3-33n^2-18n-4)-\lambda_0(2n-1)^{-1}-\lambda_1(7n^2-7n+4)(6n-3)^{-1}\\
&-\mu_0-\tfrac{1}{2}\mu_1(2n^3-3n^2+9n-4)]^2+4[\lambda_0+\lambda_1(n^2-n+1)]^2n(n-1)(2n-1)^{-2}\}^{1/2} ,
\end{aligned} \tag{5b}$$

$$\begin{aligned}
E(J=n+1)={}&B_0(n^2+3n+3)+B_1(n^4+6n^3+19n^2+30n+18)+B_2(n^6+9n^5+48n^4+153n^3+279n^2+270n+108)\\
&-\tfrac{1}{3}\lambda_0-\tfrac{1}{3}\lambda_1(n^2+3n+6)-\tfrac{1}{2}\mu_1(7n^2+21n+18)-\{[B_0(2n+3)+B_1(4n^3+19n^2+32n+19)\\
&+B_2(6n^5+45n^4+152n^3+279n^2+270n+108)-\lambda_0(2n+3)^{-1}-\lambda_1(7n^2+21n+18)(6n+9)^{-1}\\
&-\mu_0-\tfrac{1}{2}\mu_1(2n^3+9n^2+21n+18)]^2+4[\lambda_0+\lambda_1(n^2+3n+3)]^2(n+1)(n+2)(2n+3)^{-2}\}^{1/2} .
\end{aligned} \tag{5c}$$

TABLE I. Observed and calculated frequencies of oxygen lines (GHz).

Transition n, J [→]	n', J'	Observed frequency[a]	Calculated frequency
1,2	1,1	56.264 778(M) 56.264 766(W)	56.264 758
3,4	3,3	58.446 600(M) 58.446 580(Z)	58.446 580
5,6	5,5	59.590 978(Z)	59.590 979
7,8	7,7	60.434 776(Z)	60.434 778
9,10	9,9	61.150 570(Z)	61.150 567
11,12	11,11	61.800 169(W) 61.800 155(Z)	61.800 167
13,14	13,13	62.411 223(Z)	62.411 234
15,16	15,15	62.996 6(H)[b]	62.997 999
17,18	17,17	63.568 520(Z)	63.568 542
19,20	19,19	64.127 777(W)	64.127 790
21,22	21,21	64.678 2(H)[b]	64.678 920
23,24	23,23	65.224 12(Z)	65.224 076
25,26	25,25	65.764 744(W)	65.764 760
1,0	1,1	118.750 343(M)	118.750 330
3,2	3,3	62.486 255(Z) 62.486 255(M)	62.486 267
5,4	55,5	60.306 044(Z)	60.306 065
7,6	7,7	59.164 215(Z)	59.164 211
9,8	9,9	58.323 885(Z)	58.323 883
11,10	11,11	57.611 4(H)[b]	57.612 492
13,12	13,13	56.968 180(W)	56.968 214
15,14	15,15	56.363 393(W)	56.363 397
17,16	17,17	55.783 819(W)	55.783 805
19,18	19,19	55.221 372(W)	55.221 362
21,20	21,21	54.671 145(W)	54.671 141
23,22	23,23	54.129 4(H)[b]	54.129 962
25,24	25,25	53.599 4(H)[b]	53.595 682
27,26	27,27	53.066 8(Wa)	53.066 802
1, 1	3, 3	430.985 277(M)	430.985 276
13,13	15,15	2 496.283 (E)	2 496.283
21,21	23,23	3 865.81(E)	3 865.810

[a] (E) See Ref. 12, (H) see Ref. 7, (M) see Ref. 11, (W) see Ref. 6, (Wa) see Ref. 10, (Z) see Ref. 5.

[b] Line not included in fit.

III. DETERMINATION OF MOLECULAR PARAMETERS

An unweighted nonlinear least-squares program by Marquadt[14] was employed to fit 25 accurately measured microwave frequencies and three (indirectly) measured submillimeter and infrared frequencies to Eqs. (5a)-(5c). The variance of measurements estimated from the 28 residuals and seven parameters is

$$6.39\times 10^{-3}\ (\mathrm{MHz})^2/(28-7) = 3.04\times 10^{-4}\ (\mathrm{MHz})^2 .$$

The results of our best fit are given in Table I, and the values of the molecular parameters are given in Table II. Other less accurately measured microwave frequencies, including that by Waters,[10] are also shown in Table I.

TABLE II. Molecular parameters of oxygen molecule (GHz).

Parameter	Wilheit and Barrett	Butcher et. al.	Present Work
B_0	43.100 589	43.100 59(27)	43.100 518(3)[a]
B_1	-1.4×10^{-4}	$-1.454\ (4)\times 10^{-4}$	$-1.449\,629(9)\times 10^{-4}$
B_2	....		$-1.57\ (11)\times 10^{-10}$
λ_0	59.501 346		59.501 342(7)
λ_1	5.845×10^{-5}		$5.847(3)\times 10^{-5}$
μ_0	−0.252 591 7		−0.252 586 5(10)
μ_1	-2.455×10^{-7}		$-2.464(20)\times 10^{-7}$

[a] The statistical uncertainties quoted are approximately two standard deviation limits and do not include explicitly experimental uncertainties of the frequency measurements. The standard deviations were estimated from the last iteration of the nonlinear fitting procedure based upon Taylor-series expansion about the estimated values.

To achieve greater comparability with the fit of Wilheit and Barrett, the three indirect measurements are excluded and the variance of the measurements becomes (approximately)

$$6.39\times 10^{-3}\ (\mathrm{MHz})^2/(25-7) = 3.55\times 10^{-4}\ (\mathrm{MHz})^2 .$$

The corresponding variance obtained from Table I of Wilheit and Barrett's paper for the same 21 lines and four parameters is

$$8.5\times 10^{-3}\ (\mathrm{MHz})^2/(21-4) = 5.05\times 10^{-4}\ (\mathrm{MHz})^2 .$$

Not only is our fit better for the microwave lines, but also our values for the molecular parameters should be more reliable, since infrared data were included.

IV. DISCUSSION OF ROTATIONAL CONSTANTS

The values we obtained for B_0, B_1, and B_2 are essentially the same as those obtained by Evenson and Mizushima.[12] These values are considerably different from those proposed by Babcock and Herzberg,[15] but reanalysis[16] of their data showed that the values they originally proposed should be revised, and the final values agreed with ours within their experimental accuracy. Recently Butcher, Willetts, and Jones[17] measured the pure rotational Raman spectra of oxygen and proposed $B_0 = 43.10063 \pm 0.00027$ and $B_1 = (-1.454 \pm 0.004)\times 10^{-4}$ GHz. They did not, however, include corrections to the rotational triplet levels due to λ_1 and μ_1. The corrected values are given in Table II and are also in good agreement with our values.

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Spin-Change Frequency Shifts in H-H Collisions

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Accurate calculations of the frequency-shift cross section for collisions of two hydrogen atoms are presented for a range of temperatures.

The relative populations of the hyperfine levels of atomic hydrogen are controlled by spin-change processes occurring in collisions of two hydrogen atoms.[1,2] These processes are important in the theory of the hydrogen maser.[3-5] Crampton[5] observes that knowledge of the spin-change and frequency-shift cross sections are important in setting the limit of accuracy of the hydrogen maser as a spectroscopic tool and as a primary frequency standard. Cross sections for H-H collisions have been calculated previously[1-3,6-9] but they either did not take proper account of the nuclear symmetry or used potential-energy curves of uncertain accuracy. The interaction potentials corresponding to the approach of two hydrogen atoms in their ground states $X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ are now known to high precision.[10] These potentials have been used by Allison and Dalgarno[11] to calculate the rate coefficients for spin change. These calculations have been extended to give precise values of the spin-change and frequency-shift cross sections over a broad range of temperatures.

The spin-change and frequency-shift cross sections can be written[5]

$$\sigma^{\pm}(k)=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2(\eta_l^g-\eta_l^u)[1-(-1)^{l+(1/2)\pm(1/2)}]$$

and

$$\lambda^{\pm}(k)=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin 2(\eta_l^g-\eta_l^u)[1-(-1)^{l+(1/2)\pm(1/2)}]\ ,$$

where $k=\mu v/\hbar$, μ is the reduced mass, v is the relative velocity, and η_l^g, η_l^u are the phase shifts corresponding to the elastic scattering of two hy-

TABLE I. Values of the spin-change and frequency-shift cross sections for various temperatures.

T (°K)	$\bar{\sigma}^+$ (Å^2)	$\bar{\sigma}^-$ (Å^2)	$\bar{\lambda}^+$ (Å^2)
10	1.9	1.8	−27.3
20	5.6	9.9	−34.8
30	9.3	16.8	−33.0
40	12.5	20.9	−29.3
60	16.8	24.5	−22.0
80	19.1	25.9	−16.2
100	20.5	26.3	−11.7
125	21.6	26.3	− 7.5
150	22.2	26.0	− 4.4
175	22.6	25.7	− 2.2
200	22.8	25.4	− 0.4
225	22.8	25.0	1.0
250	22.8	24.7	2.1
275	22.8	24.4	3.0
300	22.7	24.2	3.8
325	22.6	23.9	4.5
350	22.5	23.7	5.1
400	22.3	23.2	6.0
450	22.1	22.8	6.7
500	21.9	22.4	7.3
600	21.5	21.8	8.0
700	21.1	21.3	8.5
800	20.8	20.9	8.8
900	20.6	20.6	9.1
1000	20.3	20.3	9.3