ELECTRON MICROSCOPY OF METEORITIC AND ARTIFICIALLY SHOCKED GRAPHITE*

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Samples of graphite, partly converted to diamond by shock, and meteoritic graphite were studied by transmission electron microscopy. The shocked graphite remained in the form of single crystals and was mildly deformed while the diamond which had formed was anhedral and polycrystalline. The meteoritic graphite contained minor amounts of troilite (FeS) and elemental sulfur but no detectable carbon phase other than graphite.

As an adjunct to an x-ray crystallographic study of meteoritic diamonds (*1*) we have studied the morphology of the phases present in meteoritic graphite, and in graphite which has been artificially shocked at pressures high enough (300 kbar) to produce diamond (*2*).

Samples of the starting material, high-purity graphite (*3*), as well as the resulting shock-product, and graphite from the interior of a 1.1-g graphite nodule from the Canyon Diablo iron meteorite were crushed to 100 mesh. Slurries in ethanol were then placed in an ultrasonic generator for 5 minutes to disperse the sample uniformly. The suspensions were placed on Formvar, collodion, or carbon substrates for examination in a Hitachi HU-11 electron microscope. Phases were identified by electron diffraction of selected areas with gold and palladium as standards.

Figure 1*a* shows a typical graphite-diamond intergrowth from the artificially shocked graphite. All of the diamonds formed in this manner were anhedral and polycrystalline. The graphite flakes seemed mildly deformed although they remained single crystals. Figure 1*b* shows a typical graphite flake from the starting material.

In both the starting material and shock product the only other phase that we found was in the

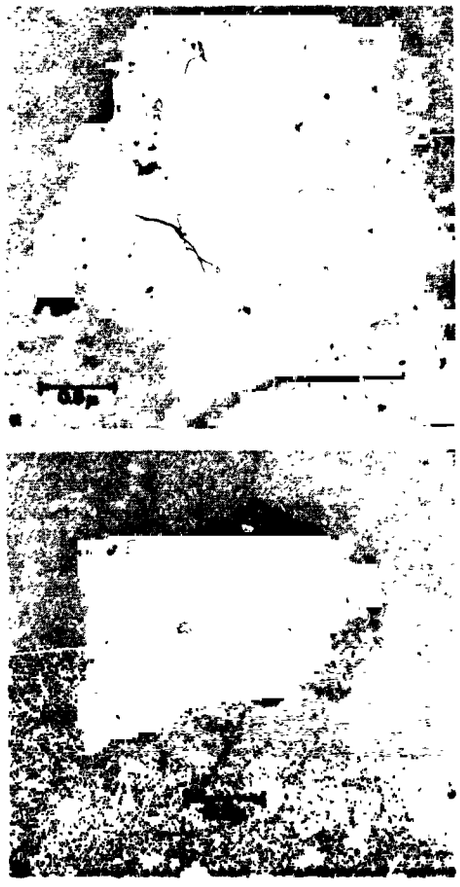

FIGURE 1.—(a) Diamond-graphite intergrowth in artificially shocked graphite. Note the anhedral morphology of the larger diamond grains (D). (b) Typical flake from the graphite starting material. The texture of this flake may be compared with that of the untransformed graphite in (a).

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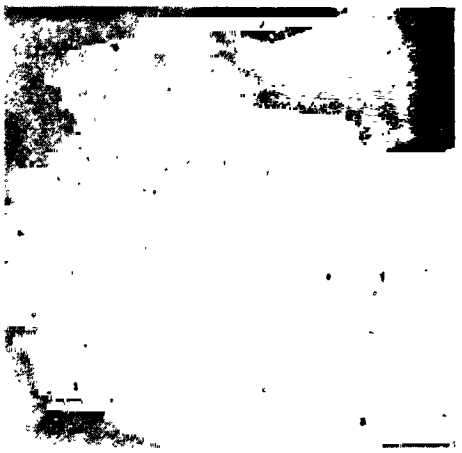

FIGURE 2.—Unidentified species present in both starting material and shock product. The cell dimension of these cubes is similar to that of the "carbon II" phase reported by Aust and Drickamer (4.)

form of euhedral cubes (Fig. 2) which were single crystals of uncertain origin. The cell dimension of these simple cubic crystals ($\alpha_0 = 5.55$ Å) corresponds very closely to that of the "carbon II" phase ($\alpha_0 = 5.545$ Å) reported by Aust and Drickamer (*4*). Inasmuch as the cubes were present in very small numbers ($<<1$ percent) in both the starting material and product we cannot say that they were produced by shock or, in fact, that they were composed of carbon. It seems very unlikely that some extraneous material would possess exactly the same cell dimension and crystallographic habit as "carbon II". Yet the cubes' euhedral appearance, the general perfection of these crystals, and their low abundance suggest that they were contaminants and not shock-formed. It could also be that these cubes were, indeed, "carbon II" which had grown relatively slowly during preparation of the original artificial graphite block. Unfortunately, all three alternatives (contamination, shock-formation, or slow growth) seem equally unlikely and it is impossible to decide among them with the available data.

The anhedral morphology of the artificial diamond might be expected from the short time available for crystal growth under the experimental shock conditions. Shocks generated during asteroidal collision (*1*) on the other hand, no doubt were of longer duration and might well be expected to result in the formation of subhedral diamond grains. These grains would probably be polycrystalline aggregates, since the shock-induced conversion of graphite to diamond apparently proceeds by a mechanism other than the orderly diffusion and addition of carbon atoms to diamond nuclei (*1*, *2*).

X-ray fluorescence analysis of the interior of the Canyon Diablo nodule indicated the presence of only iron and sulfur. The only carbon phase detected was normal graphite. The cubic phase seen in the starting material and shock product was not observed in the Canyon Diablo nodule.

The sulfur in the Canyon Diablo material apparently exists in two forms; as free rhombic sulfur and as troilite (FeS). Figure 3*a* shows anhedral single crystals of sulfur in a graphite matrix at an electron accelerating voltage of 75 kv. At 100 kv, the normal operating voltage

FIGURE 3.—(a) Sulfur (S), graphite mixture from Canyon Diablo (75-kv electrons). (b) The same area examined with 100-kv electrons. The higher accelerating voltage has sufficiently increased the temperature to melt the sulfur grains.

in these studies, the temperature reached was high enough to melt the sulfur (m.p. 113°C), and further aided in its identification (Fig. 3*b*). The troilite in the graphite nodule was identified by both x-ray and electron diffraction. It was present in amounts greater than about 5 percent while the sulfur was present in lesser amounts (about 2 percent).

The coexistence of troilite and elemental sulfur has been observed previously in Type I carbonaceous chondrites (*5*) although in these meteorites there is considerably more sulfur than troilite. Free sulfur has not previously been reported in iron meteorites. It may be that the sulfur was formed by terrestrial weathering of the troilite, the iron thus liberated forming amorphous limonite (*6*). An alternative is that these minerals are preterrestrial. If this was the case it is expected that the S^{32}/S^{34} ratios in the troilite and sulfur may differ.

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6. We thank PROF. PAUL RAMDOHR for pointing out this possibility.
7. This study was carried out, in part, while M. E. LIPSCHUTZ was in the U.S. Army at the Goddard Space Flight Center. We thank PEDRO C. SARMIENTO of the Goddard Space Flight Center for his valuable assistance, and P. S. DECARLI (Stanford Research Institute) and E. P. HENDERSON (U.S. National Museum) for providing samples. One of us (M.E.L.) thanks the National Science Foundation for a postdoctoral fellowship at Bern, and the Schweizerischen Nationalsfonds.

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A.C. CONDUCTIVITY OF A PLASMA*

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This paper computes the electrical conductivity of a fully ionized, spatially homogeneous plasma under the influence of a uniform, periodically alternating electric field. The velocity distribution of the electrons is determined by solving the linearized Fokker-Planck equations. All the terms in the collision integral are retained, including those representing electron-electron interactions. The resultant values of conductivity is expected to be valid in the range of frequencies from zero to below the plasma frequency.

I. INTRODUCTION

The purpose of this paper is to calculate the a.c. conductivity of a spatially homogeneous plasma using the Fokker-Planck equation. The d.c. conductivity of a plasma has been calculated in the well-known works of COHEN *et al.* (1950) and SPITZER Jr. and HÄRM (1953). Their results are in good agreement with the later experimental works of LIN *et al.* (1955). BERNSTEIN and TREHAN compute the a.c. conductivity assuming a Lorentz gas model (1960). The a.c. conductivity of a real gas should approach that of a Lorentz gas at high frequencies (see detailed discussions in Section 4). Toward lower frequencies their departure is expected to increase so that their ratio becomes nearly 2 in the d.c. limit, in accordance with COHEN *et al.* and SPITZER and HÄRM. The recent works on a.c. conductivity by DAWSON and OBERMAN (1962) consider the time variation of the two-particle distribution, which is necessary when dealing with a.c. currents of ultra-high frequencies. However, the domain of applicability of their work is limited to frequencies much higher than the collision frequency. Thus, a more precise calculation for the low and intermediate range of ω appears desirable and we proceed to do this in accordance with methods to be described in the next section. After completion of most of the numerical work, a paper by ROBINSON and BERNSTEIN (1962) came to our attention. They computed the a.c. conductivity using a variational technique. Our results obtained by direct integration of the Fokker-Planck equation will be compared to theirs in Section 4.

We begin with the Boltzman equation:

$$\frac{\partial f_i}{\partial t}+\mathbf{v}\cdot\frac{\partial f_i}{\partial \mathbf{r}}=\frac{F}{m}\cdot\frac{\partial f_i}{\partial \mathbf{v}}+\left(\frac{\delta f_i}{\delta t}\right)_c \qquad (1)$$

where f_i is the distribution function of particles of type i, $\left(\frac{\delta f_i}{\delta t}\right)_c$ is the change of f_i produced by collisions.

Equation (1) is deduced from Liouville theorem to describe a many-particle system under two assumptions:

(i) That the characteristic dimensions of the inhomogeneities are much larger than the average impact parameter for the particles participating in the collision.

(ii) That the characteristic time variation of the process is much longer than the duration of an average collision, or in other words, a collision is completed and the correlation function is 'relaxed' before the distribution function itself makes any appreciable change.

It should be noted here that the term 'duration of collision' is different from the so-called 'collision time'; collision time is the time between two collisions. For particles interacting through long-range forces, this time may be regarded as the time in which deflexions gradually deflected the considered particle by 90°. Duration of collision is the time during which an interaction takes place. In a plasma it is of the order ω_p^{-1}. In Fig. 1 a

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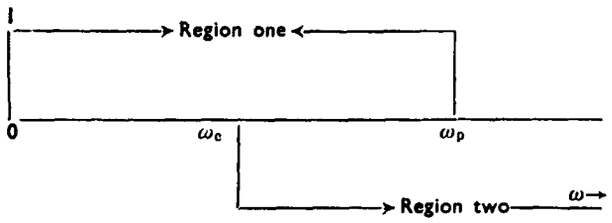

FIGURE 1.—The ranges of validity computed a.c. conductivities. The values of a.c. conductivity obtained in this paper is valid in region one. When omega exceeds ω_c—region two—the values calculated by Dawson and Oberman begin to be valid. Here ω_c is the collision frequency, ω_p is the plasma frequency.

time-scale diagram is drawn, and the validity of our calculation and those of DAWSON and OBERMAN are indicated.

The explicit expression of $\left(\frac{\delta f_i}{\delta t}\right)_c$ depends on the nature of the interaction force. In a fully ionized plasma, the particles interact through the long-range Coulomb forces. The cumulative effect of 'weak' deflexions resulting from the relatively distant collisions outweighs the effect of occasional large deflexions due to relatively close collisions, so one may neglect the contribution by those very close encounters (COHEN *et al.*)—encounters which result in deflexions of 90° or larger.

Also, the effect of distant particles lying outside the Debye length λ_D may be neglected because of the shielding of inner particles. Thus, in the computations of $\left(\frac{\delta f_i}{\delta t}\right)_c$, it is only necessary to consider the collisions with impact distance intermediate between λ_D and b_0, where $b_0=\frac{e^2}{KT}$ is the impact parameter yielding a 90° deflexion. The effects of these collisions are cumulative, and the total deflexion produced in an interval of time is similar to that of the Brownian motion; hence, one may expand $\left(\frac{\delta f_i}{\delta t}\right)_c^2$ in powers of $[\Delta \mathbf{v}]$, where $[\Delta \mathbf{v}]$ is the average velocity change due to collisions (COHEN *et al.*, CHANDRASEKHAR, 1943). This procedure leads to the following Fokker–Planck collision integral (ROSENBLUTH *et al.*, 1957):

$$\left(\frac{\delta f_i}{\delta t}\right)=\Gamma_i\left\{-\frac{\partial}{\partial \mathbf{v}}\left(f_i\frac{\partial h_i}{\partial \mathbf{v}}\right)+\frac{1}{2}\frac{\partial^2}{\partial \mathbf{v}\partial \mathbf{v}}\left(f_i\frac{\partial^2 g}{\partial \mathbf{v}\partial \mathbf{v}}\right)\right\} \quad (2)$$

where

$$h_i=\sum_j\frac{m_i+m_j}{m_j}\int d\mathbf{v}' f_j(\mathbf{v}')\,|\mathbf{v}-\mathbf{v}'|^{-1} \quad (3)$$

$$g=\sum_j\int d\mathbf{v}' f_j(\mathbf{v}')\,|\mathbf{v}-\mathbf{v}'| \quad (4)$$

and

$$\Gamma_i=\frac{4\pi z^2 e^4}{m_i^2}\ln\frac{m_i m_j v_{th}^2 \lambda D}{2(m_i+m_j)e^2}. \quad (5)$$

The summation in h_i and g sums over all species, m_i is the mass of the i-th species, e is the electronic charge, $\lambda_D=\left(\frac{KT}{4\pi ne^2}\right)^{\frac{1}{2}}$ is the Debye length, and v_{th} is the relative thermal velocity.

In this paper we consider only plasma with singly-charged ions. The extension of the present method to those with multiply-charged ions is straightforward.

2. DERIVATION OF EQUATIONS AND FORMULAE

If the distribution function f has an azimuthal symmetry about a certain axis, then, following ROSENBLUTH *et al.*, the collision term may be written down explicitly in spherical polar co-ordinates in velocity space:

$$\begin{aligned}\left(\frac{\delta f_i}{\delta f}\right)_c=\Gamma_i\Bigg\{&-v^{-2}\frac{\partial}{\partial v}\left[f_i v^2\frac{\partial h_i}{\partial v}\right]-v^{-2}\frac{\partial}{\partial \mu}\left[f_i(1-\mu^2)\frac{\partial h_i}{\partial \mu}\right]\\&+(2v^2)^{-1}\frac{\partial^2}{\partial v^2}\left[f_i v^2\frac{\partial^2 g}{\partial v^2}\right]\\&+2(v^2)^{-1}\frac{\partial^2}{\partial \mu^2}\Bigg[f_i\Bigg\{v^{-2}(1-\mu^2)^2\frac{\partial g^2}{\partial \mu^2}\\&+v^{-1}(1-\mu^2)\frac{\partial g}{\partial v}-v^{-2}\mu(1-v^2)\frac{\partial g}{\partial \mu}\Bigg\}\Bigg]\\&+v^{-2}\frac{\partial^2}{\partial \mu\partial v}\left[f_i(1-\mu^2)\left\{\frac{\partial^2 g}{\partial \mu\partial v}-v^{-1}\frac{\partial g}{\partial \mu}\right\}\right]\\&+(2v^2)^{-1}\frac{\partial}{\partial v}\Bigg[f_i\Bigg\{-v^{-1}(1-\mu^2)\frac{\partial^2 g}{\partial \mu^2}-2\frac{\partial g}{\partial v}\\&+2\mu v^{-1}\frac{\partial g}{\partial \mu}\Bigg\}\Bigg]+(2v^2)^{-1}\frac{\partial}{\partial \mu}\Bigg[f_i\Bigg\{v^{-2}\mu(1-\mu^2)\frac{\partial^2 g}{\partial \mu^2}\\&+2\mu v^{-1}\frac{\partial g}{\partial v}+2v^{-1}(1-\mu^2)\frac{\partial^2 g}{\partial \mu\partial v}-2v^{-2}\frac{\partial g}{\partial \mu}\Bigg\}\Bigg]\Bigg\}\end{aligned} \quad (6)$$

where $\mu=\cos\theta$ is the direction cosine between $\mathbf{v}$ and $\mathbf{E}$. Equation (6) is an exact expression of the Fokker–Planck equation in spherical co-ordinates for a distribution function with azimuthal symmetry.

We assume that the system is subject to a weak electric field $\mathbf{E}_0 e^{i\omega t}$ whose direction lies along z-axis. Then following CHAPMAN and COWLING (1939) and SPITZER Jr. we expand f_i in a power series of E:

$$f_i(\mathbf{v},t)=f_i^{(0)}(v)+E_0 f_i^{(1)}(\mathbf{v},t)+E_0^2 f_i^{(2)}(\mathbf{v},t)+\cdots \quad (7)$$

where $f_i^{(0)}(v)$ is a time-independent Maxwellian distribution and $f^{(1)}(\mathbf{v},t)$, $f^{(2)}(\mathbf{v},t),\cdots\cdots$ are the perturbed part due to applied electric field. When a steady state has been reached and no transient current exists, the time-dependent part of $f_i^{(j)}(\mathbf{v},t)$ must be proportional to $e^{i\omega t}$. Since the average energy imparted to the electrons between encounters is small compared with their kinetic energy, the velocity-dependent part of $f_i^{(j)}(\mathbf{v},t)$ can be written as $e^{-(m_i v^2/2kt)}D_i^{(j)}(v)\mu$. Therefore, we have

$$f_i^{(j)}(\mathbf{v},t)=\frac{m^{3/2}}{(2\pi KT)^{3/2}}e^{-m_i v^2/2KT}D_i^{(j)}(v)\mu e^{i\omega t}. \quad (8)$$

Combining equations (1), (6) and (7) keeping only terms linear in E_0, we obtain

$$\frac{\partial f_i^{(1)}}{\partial t}+\frac{e}{m_i}e^{i\omega t}\mathbf{E}_0\frac{\partial}{\partial \mathbf{v}}f_i^{(0)}=\left(\frac{\delta f_i^{(1)}}{\delta t}\right)_c \quad (9)$$

where $(\delta f_i/\delta t)_c{}^{(1)}$ is the linearized Fokker-Planck collision integral.

Since the ions' contribution to electric current is negligible compared to electrons, we will consider only electron distributions and drop the subscript i in the distribution function hereafter.

Substituting equation (8) into equation (9) we find, after some algebraic manipulations, the following second-order linear integral-differential equation:

$$D''(\chi)+P(\chi)D'(\chi)+Q(\chi)D(\chi)=R(\chi)+S(\chi) \quad (10)$$

where

$$P(\chi)=-2\chi-\frac{1}{\chi}+\frac{2\chi^2\Phi'(\chi)}{H(\chi)} \quad (11)$$

$$Q(\chi)=\frac{-iB\chi^3+2(1+\Phi=2\chi^3\Phi')}{H(\chi)}+\frac{1}{\chi^2} \quad (12)$$

$$R(\chi)=-\frac{2d\chi^4}{H(\chi)}-\frac{8(2\cdot 4\chi^6-2\chi^4)}{3\pi^{1/2}H(\chi)}I_0(\infty) \quad (1\upsilon)$$

$$S(\chi)=\frac{16}{3\pi^{1/2}H(\chi)}\{\chi I_3(\chi)-1\cdot 2\chi I_5(\chi) -\chi^4 I_0(\chi)(1-1\cdot 2\chi^2)\} \quad (14)$$

$$\Phi(\chi)=\int_0^\chi e^{-y^2}dy \quad (15)$$

$$H(\chi)=\Phi(\chi)-\chi\Phi'(\chi) \quad (16)$$

$$I_n(\chi)=\int_0^\chi y^n D(y)e^{-y^2}dy \quad (17)$$

$$I_0(\infty)=\int_0^\infty D(y)e^{-y^2}dy \quad (18)$$

with

$$\alpha=-E_0KT/\pi e^3 n\ln\lambda \qquad \lambda=\lambda_D/b_0$$

$$\chi=v\Big/\left(\frac{2KT}{m}\right)^{1/2} \qquad B=\frac{4\sqrt{2}\lambda\omega}{\omega_p\ln\lambda}=\frac{\omega}{\omega_c},$$

where ω_c is approximately the 90° deflexion time of a particle with thermal velocity. When $\omega=0$, equation (10)* reduces to equation (8) of SPITZER Jr. which considers d.c. electric conductivity.

In a d.c. electric field, the electrons are not accelerated in a steady state. Hence, the inertia force term is zero and $I_0(\infty)=\frac{3\pi^{\frac{1}{2}}}{8}\alpha$.

3. SOLUTION OF EQUATION

Equation (10) is a linear integral-differential equation whose unknown $D(\chi)$ is a complex function of a real variable. The present section will discuss the method of its solution. As will be evident in what follows, the procedure for numerical integration is far from straightforward.

On the one hand, we encounter the problem of the instability of the solution at small and at large χ. Because of the existence of singularities in equation (10) at $\chi=0$ and at $\chi=\infty$, a slight deviation of $D(\chi)$ at either small or large χ, tends to be built up quite rapidly. In order to obtain a physically acceptable solution, it is required that $D(\chi)$ does not approach infinity too fast, leading to infinite conductivities. The starting value of D at small χ can be obtained by means of a series solution. Because of the instability, we cannot proceed to integrate in a step-wise manner. To overcome this difficulty, we adopted a scheme

*Note that $I_0(\infty)$ is essentially the total change of momentum of electrons arising from electronion interactions. Since the mutual electronic interaction cannot change the total momentum of the electrons, $I_0(\infty)$, by Newton's second law, must equal the total force exerted on the electrons by the applied field minus the inertia force of electrons. This relation gives us:

$$I_0(\infty)=\frac{3\pi^{\frac{1}{2}}}{8}\alpha-\frac{iB}{2}I_3(\infty).$$

used by COHEN *et al.* We shall refer to their paper for full details.

On the other hand, we note that $I_0(\infty)$ is no longer a known quantity as it is in the case of d.c. conductivity; it depends on the solution $D(\chi)$ itself. We proceed as follows: Since we want conductivities at different frequencies, it is necessary to obtain solutions for different values of the parameter B. We begin with a small value $B=0{\cdot}05$. Using an $I_0(\infty)$ taken from the d.c. case, i.e. $I_0(\infty)=0{\cdot}655$, we obtain a solution to equation (10) from which we get a new $I_0(\infty)$. Next, we pass on to $B=0{\cdot}1$ using the $I_0(\infty)$ obtained for the previous B. In this way, we proceed to ever-increasing values of B, until the initial adopted $I_0(\infty)$ and the final calculated $I_0(\infty)$ differ by no more than 2 percent. This occurs at $B=1{\cdot}37$. From this point on, we resort to a method of systematic trials. The initial and final $I_0(\infty)$ for all values of B agree to within 2 percent, which is considered sufficiently accurate for the present purposes.

4. RESULTS AND DISCUSSION

The current is given by

$$\mathbf{J}=-e\int \mathrm{d}\mathbf{v}\mathbf{v}f_1[(\mathbf{v},t)=AE_0e^{i\omega t}I_3(\infty) \qquad (19)$$

where

$$I_3(\infty)=\int_0^\infty \chi^3 D(\chi)\mathrm{e}^{-x^2}\mathrm{d}\chi$$

$$A=\frac{2}{3}\frac{(2KT)^{3/2}}{\pi^{3/2}m^{1/2}e^2\ln\lambda}. \qquad (20)$$

Since $J=\sigma E$, we have the complex conductivity

$$\sigma=AI_3(\infty), \qquad (21)$$

the impedance

$$Z=\frac{1}{AI_3(\infty)}=\frac{c}{I_3(\infty)}, \qquad (22)$$

the resistance

$$R=\frac{1}{A}\frac{ReI_3(\infty)}{|I_3(\infty)|^2}=\frac{cReI_3(\infty)}{|I_3(\infty)|^2}, \qquad (23)$$

and the reactance

$$X=\frac{1}{A}\frac{ImI_3(\infty)}{|I_3(\infty)|^2}=\frac{cImI_3(\infty)}{|I_3(\infty)|^2}, \qquad (24)$$

with

$$c=\frac{1}{A}=\frac{3}{2}\frac{1}{(2KT)^{3/2}}\pi^{3/2}m^{1/2}e^2\ln\lambda.$$

It may be remarked here that the a.c. conductivity depends on three factors:

(i) The inertia of the conducting electrons.
(ii) The mutual interaction among electrons and ions.
(iii) The mutual interaction among electrons themselves.

The mutual electronic interactions have no direct effect on conductivity since the total change of momentum due to such interactions is zero. Nevertheless, they alter the distribution of electrons and thereby modify the effect which electron-ion collisions and electron inertia have in impeding the current. When ω is small, the conductivity is primarily determined by collisions. The inclusion of electron-electron interactions reduces the conductivity by a factor of approximately two. As ω increases and becomes of order ω_c, this effect becomes less and less important because there is then insufficient time in each a.c. cycle to allow an effective modification of the distribution by electron-electron interactions. When ω well exceeds ω_c, we may neglect this effect and $D(\chi)$ reduces to

$$D_i(\chi)=\frac{\chi^4}{1+\frac{iB}{2}\chi^3} \qquad (25)$$

and the corresponding conductivity becomes

$$\sigma_i(\chi)=A\int_0^\infty \frac{\chi^7\mathrm{e}^{-x^2}}{1+\frac{iB}{2}\chi^3}\mathrm{d}\chi \qquad (26)$$

which is just the a.c. conductivity of a Lorentz gas (BERNSTEIN and TREHAN).

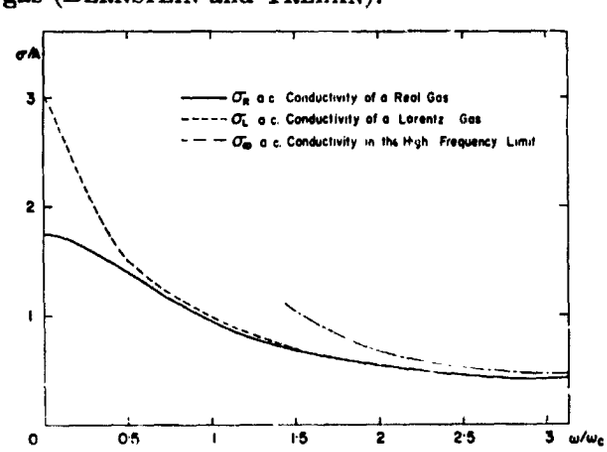

FIGURE 2.—A. C. conductivities.

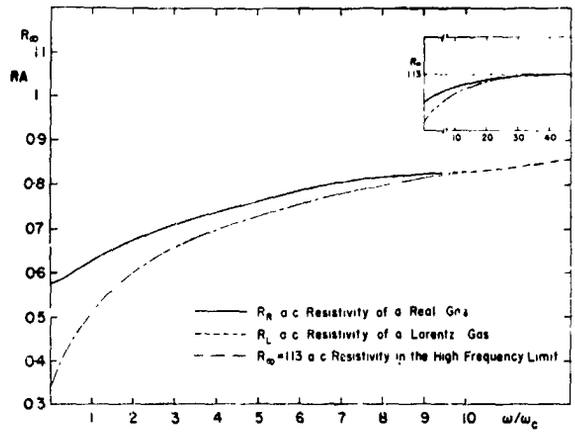

FIGURE 3.—A. C. resistivities

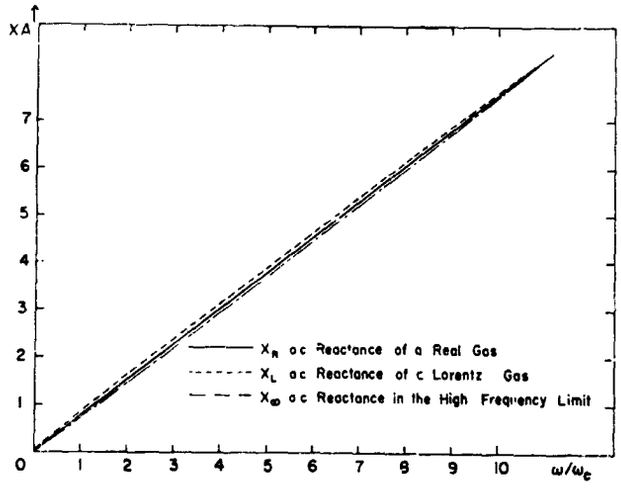

FIGURE 4.—A. C. reactances

If we further increase ω, the inertia of electrons become dominant. Then we may treat collision effect as a perturbation and obtain

$$\sigma_\infty = A\left(-\frac{3\pi^{1/2}}{4}i+\frac{2}{B^2}\right)\frac{1}{B} \tag{27}$$

$$Z_\infty = \frac{1}{A}\,\frac{4B^2}{64+9\pi B^2}(8+3\pi^{1/2}iB) \tag{28}$$

$$R_\infty = \frac{1}{A}\,\frac{32}{9\pi}\left(1-\frac{64}{9\pi B^2}\right) \tag{29}$$

$$X_\infty = \frac{1}{A}12\pi^{1/2}B\left(1-\frac{64}{9\pi B^2}\right). \tag{30}$$

In Table 1 the values of $D(\chi)$ for $B=1$ are given and compared with the corresponding values for the d.c. case obtained by SPITZER Jr. and HÄRM.

In Table 2 the resistance, the reactance and the absolute value of conductivity are given for various B from 0 to 10. For $B>10$, one may use

TABLE 1.—*Values of* $D(\chi)$ *for* $\omega=\omega_c$ *and* $\omega=0$ $\omega_c=\dfrac{\omega_p \ln\lambda}{4\sqrt{2}\lambda}$

x	$\omega=\omega_c$		$\omega=0$
	$Re[D(x)]$	$Im[D(x)]$	$D(x)$
0.10	0.0005887	−0.0002029	0.0008093
0.11	0.0009252	−0.0003438	0.001300
0.12	0.001376	−0.000542	0.001970
0.13	0.001956	−0.0008068	0.002847
0.14	0.00268	−0.001149	0.003955
0.15	0.00356	−0.00158	0.005317
0.16	0.00461	−0.00210	0.006955
0.17	0.00583	−0.00272	0.008886
0.18	0.00724	−0.00346	0.01113
0.19	0.00884	−0.00431	0.01370
0.20	0.01063	−0.00528	0.01660
0.22	0.01483	−0.00761	0.02347
0.24	0.01985	−0.01048	0.03180
0.26	0.0257	−0.0139	0.04165
0.28	0.0324	−0.0180	0.05304
0.30	0.0400	−0.0226	0.06601
0.32	0.0483	−0.0279	0.08057
0.34	0.0575	−0.0339	0.09672
0.36	0.0675	−0.0405	0.1145
0.38	0.0783	−0.0478	0.1338
0.40	0.0899	−0.0557	0.1548
0.44	0.1153	−0.07366	0.2015
0.48	0.1435	−0.09436	0.2545
0.52	0.1744	−0.1179	0.3137
0.56	0.2080	−0.1442	0.3792
0.60	0.2439	−0.1734	0.4508
0.64	0.2882	−0.2055	0.5285
0.68	0.3227	−0.2405	0.6123
0.72	0.3652	−0.2785	0.7023
0.76	0.4096	−0.3196	0.7983
0.80	0.4559	−0.3637	0.9005
0.88	0.5535	−0.4813	1.123
0.96	0.6570	−0.5718	1.371
1.04	0.7656	−0.6957	1.645
1.12	0.8782	−0.8335	1.945
1.20	0.9937	−0.9858	2.273
1.28	1.111	−1.1531	2.630
1.36	1.2290	−1.3359	3.017
1.44	1.3457	−1.5347	3.435
1.52	1.4598	−1.7500	3.887
1.60	1.5693	−1.9820	4.375
1.76	1.7657	−2.4962	5.465
1.92	1.1915	−3.0739	6.728
2.08	1.9973	−3.7049	8.190
2.24	1.9913	−4.3694	9.880
2.40	1.8852	−5.0382	11.83
2.72	1.4266	−6.2497	16.62
2.88	1.2198	−6.6809	19.53
3.04	1.3105	−6.8066	22.74
3.20	2.1113	−5.6758	26.00

TABLE 2.—*The conductivity, the resistance and the reactance of a.c. current*

ω/ω_c	σ/A		R/c		X/c	
	Real gas	Lorentz gas	Real gas	Lornetz gas	Real gas	Lorentz gas
0.0	1.734	3.0	0.577	0.333	0.0	0.0
0.05	1.729	2.880	0.577	0.340	0.045	0.70
0.1	1.713	2.653	0.577	0.354	0.089	0.130
0.15	1.687	2.430	0.578	0.367	0.134	0.185
0.2	1.651	2.233	0.579	0.380	0.178	0.236
0.25	1.608	2.061	0.58	0.393	0.223	0.285
0.3	1.561	1.913	0.582	0.404	0.267	0.332
0.35	1.510	1.784	0.584	0.415	0.311	0.377
0.4	1.458	1.671	0.587	0.425	0.354	0.421
0.45	1.406	1.572	0.590	0.434	0.397	0.465
0.5	1.354	1.483	0.593	0.443	0.440	0.508
0.55	1.303	1.405	0.597	0.452	0.482	0.550
0.6	1.255	1.334	0.600	0.460	0.525	0.592
0.65	1.208	1.270	0.603	0.467	0.567	0.634
0.7	1.164	1.212	0.607	0.475	0.608	0.675
0.75	1.122	1.159	0.610	0.482	0.650	0.716
0.8	1.082	1.111	0.614	0.488	0.691	0.756
0.85	1.045	1.066	0.617	0.495	0.732	0.797
0.9	1.009	1.025	0.620	0.501	0.773	0.807
0.95	0.976	0.987	0.624	0.507	0.813	0.877
1.0	0.944	0.952	0.627	0.513	0.853	0.916
1.1	0.886	0.889	0.634	0.524	0.934	0.996
1.2	0.834	0.835	0.640	0.534	1.013	1.074
1.3	0.786	0.785	0.645	0.544	1.094	1.159
1.4	0.743	0.741	0.750	0.553	1.172	1.230
1.5	0.721	0.702	0.657	0.561	1.222	1.308
2.0	0.560	0.557	0.672	0.599	1.588	1.693
3.0	0.408	0.398	0.711	0.655	2.335	2.453
4.0	0.313	0.305	0.734	0.696	3.086	3.207
5.0	0.255	0.248	0.766	0.728	3.842	3.960
6.0	0.214	0.211	0.784	0.754	4.601	4.710
7.0	0.183	0.182	0.790	0.776	5.380	5.460
8.0	0.162	0.161	0.796	0.794	6.08	6.21
9.0	0.144	0.143	0.814	0.810	6.69	6.81
10.0	0.130	0.129	0.830	0.824	7.51	7.6

equation (26) to compute them. The error will be within 2 percent. For $B>50$ the collisions become unimportant and equations (27)–(30) will give the correct values to within 2 percent. However, there the validity of the Fokker-Planck equation already becomes questionable and one should use DAWSON-OBERMAN'S values instead of ours.

In Table 3, the complex conductivity calculated in this paper are compared with those obtained by ROBINSON and BERNSTEIN. They showed that transport coefficients obtained from the Fokker-Planck equation should possess an extremal nature, and proceed to calculate conductivities using the variational technique. Their Table 6 gives conductivities for various values of the logarithm of ω/ω_c including very large values of ω_c. In our Table 3 only those values are included for comparison which fall within the range of validity of the Fokker-Planck equation. The discrepancy between the two results are generally within 5 percent.

TABLE 3.—*Comparison of the a.c. conductivities obtained in this paper (direct integration) with those obtained by Berstein and Robinson (variational calculation)*

ω/ω_c	*Log X* $(X=4\sqrt{2\omega/\omega_c})$	$Re\sigma/A$		$-Im\sigma/A$	
		BERNSTEIN ROBINSON	SHEN–CHEN	BERNSTEIN–ROBINSON	SHEN–CHEN
0.0	$-\infty$	1.734	1.734	0.000	0.000
0.0057	−3.0	1.734	1.734	0.004	0.002
0.0179	−2.5	1.730	1.732	0.649	0.408
0.0565	−2.0	1.705	1.722	0.154	0.151
0.179	−1.5	1.605	1.608	0.447	0.443
0.565	−1.0	0.992	0.987	0.816	0.813
0.901	−0.8	0.637	0.632	0.785	0.787
1.425	−0.6	0.357	0.353	0.645	0.649
2.261	−0.4	0.183	0.179	0.477	0.482
3.559	−0.2	0.087	0.084	0.329	0.336
5.65	0.0	0.040	0.038	0.201	0.204

We should add that our results can be readily applied to the case of conductivity in the presence of a uniform magnetic field. The addition of the magnetic field leads to equations which are entirely similar to (10). If the electric field is parallel to the magnetic field, the conductivity is not affected. If it is perpendicular to the magnetic field, the conductivity becomes $\sigma_H(\omega)\equiv\sigma(\omega+\omega_H)$, where σ is the function obtained in this paper and $\omega_H=eH/mc$.

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PARTIAL WAVE THEORY OF DIATOMIC MOLECULES, II*

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The method of expanding the wave function of diatomic molecules in a series of orbital angular momentum eigenfunctions (partial waves) is extended to two-electron homonuclear molecules. The angular momentum is a function of the Euler angles only; a symmetric choice of these angles is used which greatly facilitates the description of the exchange character of the wave function. As a result, explicit equations for the 3 dimensional "radial" functions can be derived for all the different magnetic parity, and exchange states. For Σ states the partial wave sums only go over alternate values of the angular momentum giving rise to the expectation of an even more rapidly convergent series in these cases.

I. INTRODUCTION

In a previous paper[1] as well as others,[2] the idea of expanding the wave function of a (homonuclear) diatomic molecule in a series of angular momentum eigenfunctions was introduced for the purpose of affording a very natural method of successive approximations in these problems.

Previous calculations[1,2] using this idea have almost exclusively been confined to the one-electron molecule H_2^+. In that case, the formalism is rather easily constructed, and the results are in the nature of a check as the problem is amenable to exact calculation.[3] The comparison with the exact results is nevertheless most encouraging.[1]

The main immediate goal of this approach is two-electron molecules for which there is no analytically exact solution. As a prerequisite for effecting this approach, however, it is necessary that two electron atoms be completely understood. Although the general approach to the two-electron atomic problem is quite old[4], only results for specific angular momentum states have until recently been derived. The difficulty lay in the description of the character of the wave function under the exchange of electron coordinates which becomes very complicated[4] with the original choice of Euler angles[5]. The explicitly complete solution has required a symmetrical choice of Euler angles, which Holmberg[6] has provided, and has therefore only just been carried out[7].

In section II, we very briefly review the main results of that investigation and present some additional transformation properties of the Euler angles and vector spherical harmonics which bear on the present application. In section III we describe the construction of the molecular wave functions, and in section IV we derive the radial equations. These equations couple states of different angular momentum through the potential energy, but the kinetic energy acts in the same way as in the atomic case. The new feature is, therefore, only the coupling terms of the molecular potential and this in turn depends on integrals over three vector spherical harmonics. The heart of section III is the resulting formulae for these integrals and the selection rules for its non-vanishing. This latter consideration leads to the decoupling of the Σ states according to even $(+)$ or odd $(-)l$. This decoupling is not present for other m states corresponding to the absence of the $\pm$ quantum numbers in those cases; thus the Σ states provide particularly favorable cases for the rapid convergence of the partial wave expansion.

Section V presents the zeroth-order equation for the Σ_g^+ states and discusses a specific calculation which can be related to the accuracy of this approximation and which by inference bears upon the convergence properties of the entire sequence of approximations which this paper projects.

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II. THE EULER ANGLES AND TRANSFORMATION PROPERTIES

The Schrödinger equation of a two-electron homonuclear molecule whose nuclei are considered fixed (Born-Oppenheimer approximation) will depend on the two vectors of the electrons $\mathbf{r}_1$ and $\mathbf{r}_2$ which can be measured relative to an origin defined as the midpoint between the nuclei and parametrically on the internuclear separation R_{AB}.

In place of the six coordinates $\mathbf{r}_1$, $\mathbf{r}_2$ one can introduce the three Euler angles and three residual variables; the Euler angles describe the orientation of the plane containing the two unit vectors $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$ relative to a space-fixed coordinate system (whose z-axis is by definition the internuclear axis).

The particular Euler angles we use where introduced by Holmberg[6] and have the advantage of being symmetrically disposed with respect to the

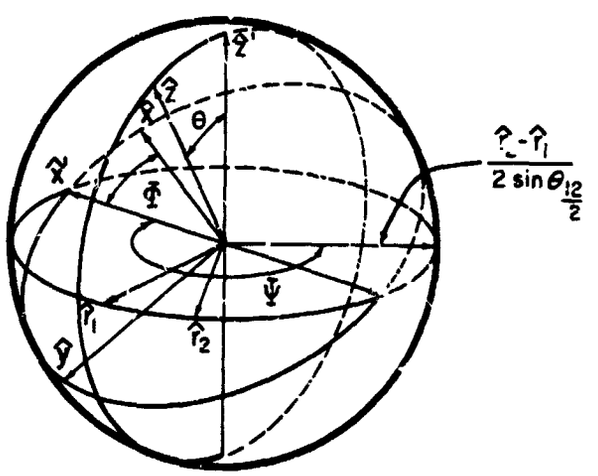

FIGURE 1.—Perspective drawing of (Holmberg's) Euler angles and the unit vectors of the problem.

two-electron. Figure 1 contains a diagrammatic representation of these angles and the unit vectors with which we shall be concerned.

The axes are defined by

$$\hat{\mathbf{z}}' = (\hat{\mathbf{r}}_1 \times \hat{\mathbf{r}}_2)/\sin\theta_{12} \tag{2.1}$$

$$\hat{\mathbf{x}}' = (\hat{\mathbf{z}} \times \hat{\mathbf{z}}')/\sin\theta \tag{2.2}$$

$$\hat{\mathbf{y}}' = \hat{\mathbf{z}}' \times \hat{\mathbf{x}}' \tag{2.3}$$

The Euler angles are obviously: θ = angle between $\hat{\mathbf{z}}$ and $\hat{\mathbf{z}}'$; Φ = angle between $\hat{\mathbf{x}}$ and $\hat{\mathbf{x}}'$; Ψ = angle between $\hat{\mathbf{x}}'$ and $(\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2)$. Trigonometric relations between these angles and the particles spherical angles have been worked out in reference 7; the reader is encouraged to familiarize himself with that discussion, although we shall attempt to make this treatment reasonably self-contained. Specifically, we shall repeat here the relation of the x, y and z components of $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$ to the Euler angles in order that the transformation properties given below can readily be checked.

$$\frac{x_1}{r_1} = \sin\vartheta_1\cos\varphi_1 = \cos\Phi\sin(\psi - \tfrac{1}{2}\theta_{12}) + \cos\theta\sin\Phi\cos(\psi - \tfrac{1}{2}\theta_{12}) \tag{2.5}$$

$$\frac{y_1}{r_2} = \sin\vartheta_1\sin\varphi_1 = \sin\Phi\sin(\psi - \tfrac{1}{2}\theta_{12}) - \cos\theta\cos\Phi\cos(\psi - \tfrac{1}{2}\theta_{12}) \tag{2.6}$$

$$\frac{z_1}{r_1} = \cos\vartheta_1 = -\sin\theta\cos(\psi - \tfrac{1}{2}\theta_{12} \tag{2.7}$$

The formulae for analogous components of $\hat{\mathbf{r}}_2$ may be obtained from the above by letting $\theta_{12} \rightarrow -\theta_{12}$. The angle θ_{12} is the angle between $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$. It is not one of the Euler angles, but rather one choice of residual coordinate, the other two usually being chosen as the two distances r_1 and r_2. The residual coordinates are often called generalized radial coordinates; an alternate choice is r_1, r_2, r_{12}, the latter being the interelectron distance.

The distinguishing feature of the Euler angles as opposed to residual coordinates is the fact that the angular momentum depends only on the Euler angles. In this connection, it is well known that square of the total orbital angular momentum, $\mathbf{M}^2$, can be conserved in atoms but not in diatomic molecules, whereas the z-component of the angular momentum, M_z, is a possible constant of the motion in both cases. A central role in the atomic problem is therefore played by the eigenfunctions of the total angular momentum $D_l^{m,k}(\theta,\Phi,\Psi)$:

$$D_l^{m,k}(\theta,\Phi,\psi) = \frac{\sqrt{2(2l+1)}}{4\pi} e^{i(m\Phi+k\psi)} d_l^{m,k}(\theta) \tag{2.8}$$

where

$$d_l^{m,k}(\theta) = (-1)^{\frac{1}{2}(|k-m|+k-m)} \frac{4\pi}{\sqrt{2(2l+1)}} N_{lmk} \sin^{|k-m|}\left(\frac{1}{2}\theta\right)\cos^{|k+m|}\left(\frac{1}{2}\theta\right) F\left(-l+\frac{\beta}{2}-1,\ l+\frac{\beta}{2},1+|k-m|,\sin^2\frac{\theta}{2}\right) \tag{2.9}$$

$$\beta = |k+m| + |k-m| + 2 \tag{2.10}$$

and

$$N_{\ell mk} = \frac{1}{(|k-m|)!}\left[\frac{(2\ell+1)}{8\pi^2}\,\frac{(\ell+\frac{1}{2}|k+m|+\frac{1}{2}|k-m|)!}{(\ell-\frac{1}{2}|k+m|-\frac{1}{2}|k-m|)!}\times\frac{(\ell-\frac{1}{2}|k+m|+\frac{1}{2}|k-m|)!}{(\ell+\frac{1}{2}|k+m|-\frac{1}{2}|k-m|)!}\right]^{\frac{1}{2}} \tag{2.11}$$

The eigenfunction character of these functions is then given by

$$\mathbf{M}^2 D_\ell^{m,k} = \hbar^2 \ell(\ell+1) D_\ell^{m,k} \tag{2.12}$$

$$\mathbf{M}_z D_\ell^{m,k} = \hbar m D_\ell^{m,k} \tag{2.13}$$

where the explicit form of $\mathbf{M}^2$ and $\mathbf{M}_z$ has been derived in reference 7 and in any case is known[8]. In the atomic problem if we are describing a state of definite orbital angular momentum ℓ with z-component m, then the wave function is at most a finite sum over the $(2\ell+1)$ function for the given ℓ and m:

$$\Psi_{\ell m}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=-\ell}^{\ell} g_\ell^{m,k}(r_1,r_2,\theta_{12}) D_\ell^{m,k}(\theta,\Phi,\psi) \tag{2.14}$$

Actually the above sum is more general than what is needed. Specifically one has an additional operation which commutes with the Hamiltonian and therefore gives rise to an additional constant of the motion. This is the operation of space inversion (called parity, p, in the atomic application[7]), usually labelled iE in molecular applications[9] corresponding to the operation $\mathbf{r}_1 \rightarrow -\mathbf{r}_1$, $\mathbf{r}_2 \rightarrow -\mathbf{r}_2$ in all cases. It turns out that only the Euler angles are involved in this transformation, and if we denote them by a three component vector, (θ, Φ, Ψ), then[7]

$$iE\begin{pmatrix}\theta\\ \Phi\\ \psi\end{pmatrix} = \begin{pmatrix}\theta\\ \Phi\\ \pi+\psi\end{pmatrix} \tag{2.15}$$

and

$$iE D_\ell^{m,k}(\theta,\Phi,\Psi) = (-1)^k D_\ell^{m,k}(\theta,\Phi,\Psi) \tag{2.16}$$

Therefore, the wave function (2.14), if it is to be an eigenfunction of iE, must be restricted to even or odd k. Since the action of the Schrödinger equation is to couple all possible $g_\ell^{m,k}$ functions for the given ℓ and m, it can be seen that the invocation of parity halves the number of functions, and thus among other things is of considerable practical utility.

In the case of diatomic molecules the invariance against rotations, except those around the z-axis, is lost. Thus according to the above arguments only the rotation quantum number m survives. The idea of the partial wave theory, then, is to expand the molecular wave function in terms of the orbital angular momentum:

$$\Psi_m = \sum_{\ell=|m|}^{\infty} \Psi_{\ell m}$$

The above sum too may be delimited according to the symmetry properties of the states we intend to describe. These symmetry operations are well known for the diatomic molecule,[9], and except for exchange, ϵ_{12}, they all involve only the Euler angles. The transformation involved in the residual variables for ϵ_{12}, is $r_1 \rightleftarrows r_2$ independent of whether the third variable is taken as θ_{12} or r_{12}.

In Table I we have summarized the transformation properties of the Euler angles and the vector spherical harmonics under some of the major symmetry operations of the two-electron homonuclear diatomic molecule.

In the next section we shall utilize these properties to construct wave functions with the desired symmetry properties. We emphasize that *not* all these properties are independent. Thus for example a full space inversion is the product of the inversion about each of the axes separately:

$$iE = \sigma_h \sigma_{vx} \sigma_{vy}$$

where the factors on the right can be written in any order. Therefore, the operation σ_h is redundant.

The effect of additional symmetry operations such as σ_v on the angular momentum eigenfunctions and variables can easily be worked out from Table I by noting, in this case, that

$$i\sigma_v = iE \cdot \sigma_v$$

Not all symmetry operations commute with M_z. Specifically σ_v does not commute with M_z. This may be easily ascertained by envisaging a vector

TABLE 1.—*Symmetry properties of the Euler angles and the angular momentum eigenfunctions.*

Transformation Property	θ	Φ	Ψ	$D_l^{m,k}$
iE space inversion (parity)	θ	Φ	$\Psi+\pi$	$(-1)^k D_l^{m,k}$
σ_h reflection through x=y plane (inversion of z-coordinates	θ	$\Phi+\pi$	$\Psi+\pi$	$(-1)^{k+m} D_l^{m,k}$
σ_{vz} reflection through z−x plane (inversion of y-coordinates)	$\pi-\theta$	$2\pi-\Phi$	Ψ	$(-1)^{l-k} D_l^{-m,k}$
σ_v, reflection through z−y plane (inversion of x-coordinates)	$\pi-\theta$	$\pi-\Phi$	Ψ	$(-1)^{l+m-k} D_l^{-m,k}$
ϵ_{12} exchange of particles*	$\pi-\theta$	$\Phi+\pi$	$2\pi-\Psi$	$(-1)^l D^{m,-k}$

*This operation also affects the residual coordinates. See text.

whose projection in the x-y plane is in the first quadrant. If first you reflect it through the y-z plane (σ_{vy}), thus putting in the second quadrant and then rotate around the z-axis by 90°, this vector will end up with a projection in the third quadrant. If first you rotate by 90°, putting it in the second quadrant, and then reflect through the y-z plane, you put it back into the first quadrant. Thus

$$[\sigma_v, M_z] \neq 0 \tag{2.19a}$$

This means that in general one can't construct simultaneous eigenfunctions of M_z and σ_v.

There is one exception to that situation, and that is Σ states.

For in that special case

$$M_z D_l^{0,k} = 0, \tag{2.17}$$

so that

$$[\sigma_v, M_z] D_l^{0,k} = 0, \tag{2.18}$$

or

$$[\sigma_v, M_z]_{m=0} = 0 \tag{2.19b}$$

We shall see in the next section that because of this fact the structure of the Σ wave function and the resulting Σ radial equations is quite different from all other states.

III. WAVE FUNCTIONS AND THE POTENTIAL ENERGY

In order to facilitate the derivation of the radial equations, it is convenient to construct an alternate set of orthonormal vector spherical harmonics which for $m=0$ are real[7]. We define

$$D_l^{(m,\varkappa)+} \equiv (\sqrt{2}+\delta_{0\varkappa}(2-\sqrt{2}))^{-1} (D_l^{m,\varkappa}+D_l^{m,-\varkappa}) \tag{3.1a}$$

$$D_l^{(m,\varkappa)-} \equiv (\sqrt{2}i)^{-1}(D_l^{m,\varkappa}-D_l^{m,-\varkappa}) \tag{3.1b}$$

The important point about these alternate sets of vector spherical harmonics is that they are eigenfunctions of exchange:

$$\epsilon_{12} D_l^{(m,\varkappa)\pm} = \pm(-1)^l D_l^{(m,\varkappa)\pm} \tag{3.2}$$

while still retaining their eigenfunction character with respect to parity, $\mathbf{M}^2$, and M_z (with eigenvalues $(-1)^\varkappa$, $\hbar^2\ell(\ell+1)$, $\hbar\, m$ respectively).

For $m \neq 0$ we have already indicated in the previous section that the correct expansion of the complete wave function is

$$\Psi_m = \sum_{l=|m|}^{\infty} {\sum_{\varkappa}}'' (f_l^{(m,\varkappa)+}(r) D_l^{(m,\varkappa)+} + f_l^{(m,\varkappa)-}(r) D_l^{(m,\varkappa)-}) \tag{3.3a}$$

The double prime on the summation indicates that every second value of the summation index (in this case $\varkappa$) is to be taken. This insures as stated, that the wave function is an eigenfunction of iE. It is precisely this property which distinguishes the homonuclear from the heteronuclear molecule. Thus there is established in the present homonuclear case two classes of solutions for a given m, one for even and one for odd $\varkappa$. These are of course the gerade and ungerade states respectively.

The radial functions $f_l^{(m,\varkappa)\pm}(r)$ are written as functions of r which is short for the generalized radial coordinates, either r_1, r_2, θ_{12} or r_1, r_2, r_{12}. The superscript indicates that the radial functions depend on the magnetic quantum number m. However the well-known degeneracy of the energy with respect to $\pm m$ indicates that the radial functions for $\pm m$ states must be simply related to each other. The relation is undefined up to a $\pm$ sign, but a consistent choice is (see below)

$$f_l^{(-m,\varkappa)\pm}(r_1,r_2,\theta_{12})=(-1)^{\beta}f_l^{(m,\varkappa)\pm}(r_1,r_2,\theta_{12})$$

The derivation of radial equations divides itself into two parts, the kinetic energy and the potential energy. The kinetic energy is diagonal with respect to ℓ and m but by no means trivial with respect to how mixes the allowable $\varkappa$ components. However, this aspect of its behaviour has been derived in detail in reference 7 and will not change in this application.

The potential energy in the atomic problem depends only on the generalized radial variables r_1, r_2, r_{12} and therefore acts as additional, completely diagonal terms in the atomic radial equations. On the other hand the molecular potential energy is precisely what destroys the spherical symmetry of the Hamiltonian. Specifically for nuclei of charge z (energy in units of rydbergs) to complete molecular potential is

$$v_{m0\ell}+\frac{2}{r_{12}}=-\frac{2z}{R_{A1}}-\frac{2z}{R_{A2}}-\frac{2z}{R_{B1}}-\frac{2z}{R_{B2}}+\frac{2}{r_{12}} \tag{3.4}$$

The last term is the interelectron repulsion and since it commutes with the angular momentum as discussed above need not be considered further. For the rest we can expand

$$V_{m0\ell}=-4z\sum_{\lambda\ \text{even}}{}''\, g_\lambda(\tfrac{1}{2}R_{AB},r_1)P_\lambda(\vartheta_1) -4z\sum_{\lambda\ \text{even}}{}''\, g_\lambda(\tfrac{1}{2}R_{AB},r_2)P_\lambda(\vartheta_2) \tag{3.5}$$

where

$$g_\lambda(x,y)\equiv\begin{cases}\dfrac{x^\lambda}{y^{\lambda+1}} & x<y\\[2ex] \dfrac{y^\lambda}{x^{\lambda+1}} & y<x\end{cases} \tag{3.6}$$

R_{AB} is the internuclear separation. The Legendre polynomials $P_\lambda(\vartheta)$ (note what we mean is eg. $P_1(\vartheta)=\cos\vartheta$ *not* $P_1(\vartheta)=\vartheta$) can further be expanded in terms of the Euler angles and θ_{12}[7]:

$$P_\lambda(\vartheta_1)=\frac{4\pi}{(2\lambda+1)^{\frac{1}{2}}}\sum_{\mu\ \text{even}}{}''\,[\alpha_\lambda^{\mu+}(\theta_{12})D_\ell^{(0,\mu)+} -\alpha_\lambda^{\mu-}(\theta_{12})D_\ell^{(0,\mu)-}] \tag{3.7a}$$

Applying ϵ_{12}, we get from the above

$$P_\lambda(\vartheta_2)=\frac{4\pi}{(2\lambda+1)^{\frac{1}{2}}}\sum_{\mu\ \text{even}}{}''\,[\alpha_\lambda^{\mu+}(\theta_{12})D_\lambda^{(0,\mu)+} -\alpha_\lambda^{\mu-}(\theta_{12})D_\lambda^{(0,\mu)-}] \tag{3.7b}$$

where

$$\alpha_\lambda^{\mu+}(\theta_{12})=(-1)^\mu P_\lambda^\mu(\pi/2)\left[\frac{(\lambda-\mu)!}{(\lambda+\mu)!}\right]^{\frac{1}{2}}\left\{\frac{\delta_{0\mu}}{\sqrt{2}} +(1-\delta_{0\mu})\cos\left(\frac{\mu}{2}\theta_{12}\right)\right\} \tag{3.8a}$$

$$\alpha_\lambda^{\mu-}(\theta_{12})=(-1)^\mu P_\lambda^\mu(\pi/2)\left[\frac{(\lambda-\mu)!}{(\lambda+\mu)!}\right]^{\frac{1}{2}}\sin\left(\frac{\mu}{2}\theta_{12}\right) \tag{3.8b}$$

The associated Legendre polynomials are understood to have the phase of Magnus and Oberhettinger[10], and their argument is understood to be inserted in the transcendental form of these functions as parenthesized above.

Since $P_\lambda(\vartheta)$ has parity $(-1)^\lambda$ and from (3.5) λ is even, it follows the sums in (3.7) go over only even μ as indicated.

The point of these expansions is that when the wave function (3.3) is substituted into the Schrödinger equation

$$H\Psi_m=E\Psi_m \tag{3.9}$$

where

$$H=T+V_{m0\ell}+2/r_{12} \tag{3.10}$$

and T is the kinetic energy, only $V_{m0\ell}$ will couple terms of different ℓ. The decompositions, Eqs. (3.7), then tell us that the coupling from a state (radial function) with quantum members ℓ, $\varkappa$, m to one with quantum numbers ℓ_f, $\varkappa_f$, m (the molecular interaction is still diagonal in m) will be governed by integrals over *three* vector spherical harmonics. Two of these angular functions come from the coupled states and one from the interaction; the integral in question is therefore a linear

combination of integrals of the form

$$\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}(D_{\ell_i}^{m,\varkappa_i})^* D_{\lambda}^{0,\mu} D_{\ell_f}^{m,\varkappa_f}\sin\theta d\theta d\Phi d\psi = \sqrt{\frac{(2\ell_i+1)(2\lambda+1)}{8\pi^2(2\ell_f+1)}}(\ell_i\lambda-m0\,|\,\ell_f-m)(\ell_i\lambda-\varkappa_i\mu\,|\,\ell_f-\varkappa_f) \quad (3.11)$$

The formula for this integral given on the *rhs* of the above equation is well known[11] in terms of the Clebsch-Gordan (C-G) coefficients. The selections for the vanishing of this integral can therefore be deduced from those of the C-G coefficients.

Consider first Σ states ($m=0$). In this case the first C-G coefficient becomes $(\ell\ \lambda\ 00/\ell'0)$. This coefficient vanishes unless $\ell+\lambda+\ell'=$even (integer). But λ is an even integer, Eq. (3.5, therefore:

$$\ell+\ell'=\text{even}$$

This says that for Σ states only radial functions of even ℓ will be coupled together and only odd ℓ states will be coupled but there will be no intermixing. Thus for Σ states the expansion of the wave function, Eq. (3.3a), separates into two classes defined by the evenness or oddness of ℓ:

$$\Psi_0=\sum_{\ell}^{''}\sum_{\varkappa}^{''}(f_\ell^{(0,\varkappa)+}(r)D_\ell^{(0,\varkappa)+} + f_\ell^{(0,\varkappa)-}(r)D_\ell^{(0,\varkappa)-}) \quad (3.12)$$

The molecular quantum numbers $\pm$ are determined by the parity of ℓ which is the eigenvalue of $i\,\sigma_{xy}$. This then constitutes the exception to the noncommutivity of σ_{xy} with M_z which was noted in Eq. (2.19).

The quantum lables of the Σ states are compiled in the entries of the following simple array:

$\varkappa$ \ ℓ	even	odd
even	gerade, +	gerade, −
odd	ungerade, +	ungerade, −

For $m\neq 0$, the relevant C-G coefficient is not necessarily zero when $\ell+\lambda+\ell'=$odd. Thus the decoupling according to even or odd ℓ ($\pm$symmetry) does not occur, corresponding to the noncommutivity of σ_y with M_z, Eq. (2.19b). Here, however, there exists a well known degeneracy in energy with respect to $\pm m$ eigenfunctions. If the eigenfunction for $+m$ is given by (3.3a) and that for $-m$ is given by

$$\Psi_{-m}=\sum_{\ell=|m|}\sum_{\varkappa}^{''}(f_\ell^{(-m)\varkappa)+}D_\ell^{(-m,\varkappa)+} + f_\ell^{(-m,\varkappa)-}D_\ell^{(-m,\varkappa)-}), \quad (3.3b)$$

the obvious question is what is the relation of the $f_\ell^{(m,\varkappa)\pm}$ to $f_\ell^{(-m,\varkappa)\pm}$. The answer to this question still resides in the same C-G coefficient, in this case in the symmetry property[11]:

$$(\ell\lambda m0\,|\,\ell'm)=(-1)^{\ell+\lambda+\ell'}(\ell\lambda\text{--}m0\,|\,\ell'-m) \quad (3.13)$$

Since $\lambda=$ even, we see the sign of the coupling of an ℓ to an ℓ' state is reversed for Ψ_{-m} relative to what it is for Ψ_m if $\ell+\ell'=$odd (i.e., ℓ and ℓ' have opposite parity). If the radial functions change sign in the same way, then the equations (and hence the eigenvalues) will in fact not change. i.e., we must have

$$f_\ell^{(-m,\varkappa)\pm}=(-1)^l f_\ell^{(m,\varkappa)\pm} \quad (3.14a)$$

This relation could be altered by a minus sign; the relation

$$f_\ell^{(-m,\varkappa)\pm}=(-1)^{\ell+m} f_\ell^{(m,\varkappa)\pm} \quad (3.14b)$$

is equally acceptable and has the advantage that the first radial function that appears in the expansion of Ψ_m will be the one which doesn't change sign when used in Ψ_{-m}.

In all cases we have by virtue of the very simple exchange property of $D_\ell^{(m,\varkappa)\pm}$, Eq. (3.2), that the complete spatial wave function Ψ_m will be symmetric (upper sign) or antisymmetric (lower sign) if the radial functions have the exchange property

$$f_\ell^{(m,\varkappa)+}\left(r_2,\ r_1,\begin{Bmatrix}\theta_{12}\\ r_{12}\end{Bmatrix}\right) = \pm(-1)^\ell f_\ell^{(m,\varkappa)+}\left(r_1,\ r_2,\begin{Bmatrix}\theta_{12}\\ r_{12}\end{Bmatrix}\right) \quad (3.15a)$$

and

$$f_\ell^{(m,\varkappa)-}\left(r_2,\ r_1,\begin{Bmatrix}\theta_{12}\\ r_{12}\end{Bmatrix}\right) = \pm(-1)^{\ell+1} f_\ell^{(m,\varkappa)-}\left(r_1,\ r_2,\begin{Bmatrix}\theta_{12}\\ r_{12}\end{Bmatrix}\right) \tag{3.15b}$$

These properties essentially halve the independent variable space over which the equations need to be integrated[7].

IV. RADIAL EQUATIONS

The foregoing discussion together with the knowledge of the kinetic energy operator[7] essentially allows us to write down the "radial" equations for arbitrary m. Specifically substituting (3.12) or (3.3a) into the Schrödinger equation, multiplying on the left by $D_\ell^{(m,\varkappa)*}$ and integrating over the Euler angles, one obtains

$$\left[L_{\theta 12}+\frac{2m}{\hbar^2}\left(E-\frac{2}{r_{12}}\right)\right]f_\ell^{(m,\varkappa)+}(r)-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\left[\left\{\frac{\ell(\ell+1)-\varkappa^2}{2\sin^2\theta_{12}}+\frac{\varkappa^2}{4}-\frac{\cot\theta_{12}}{2\sin\theta_{12}}\delta_{1\varkappa}(1-2A_\varkappa^\ell)\right\}f_\ell^{(m,\varkappa)+}(r)\right.$$
$$+(\varkappa+1)(\varkappa+2)\frac{\cot\theta_{12}}{\sin\theta_{12}}B_{\ell,\varkappa+2}f_\ell^{(m,\varkappa+2)+}(r)+\frac{\cot\theta_{12}}{4\sin\theta_{12}}\frac{(1+3\delta_{0,\varkappa-2})}{(1+\delta_{0,\varkappa-2}(\sqrt{2}-1))}\frac{A_{\varkappa-2}^\ell A_{\varkappa-1}^\ell}{\beta_{\ell\varkappa}}f_\ell^{(m,\varkappa-2)+}(r)\Big]$$
$$+\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\left[\varkappa\left(\frac{\cos\theta_{12}}{2\sin(\frac{1}{2}\theta_{12})}-\cot\theta_{12}-\frac{1}{2\sin\theta_{12}}\right)f_\ell^{(m,\varkappa)-}(r)-\varkappa\frac{\partial f_\ell^{(m,\varkappa)-}(r)}{\partial\theta_{12}}\right.$$
$$-\frac{\delta_{1\varkappa}(1-2A_\varkappa^\ell)}{2\sin\theta_{12}}f_\ell^{(m,\varkappa)-}+\frac{(\varkappa+1)(\varkappa+2)}{\sin\theta_{12}}\beta_{\ell,\varkappa+2}f_\ell^{(m,\varkappa+2)-}(r)$$
$$\left.-\frac{1}{4\sin\theta_{12}}\frac{(1-\delta_{0,\varkappa-2})}{(1+\delta_{0,\varkappa-2}(\sqrt{2}-1))}\frac{A_{\varkappa-2}^\ell A_{\varkappa-1}^\ell}{\beta_{\ell\varkappa}}f_\ell^{(m,\varkappa-2)-}(r)\right]$$
$$+\frac{2m}{\hbar^2}4\pi\sum_{\gamma_f}\sum_{j=1}^{2}\sum_{\gamma_\lambda(\text{even})}^{\prime\prime}g_\lambda\left(\frac{1}{2}R_{AB},\ r_j\right)(1-2\delta_{2j}\delta_{\epsilon_\lambda -})\alpha_\lambda^{\mu\epsilon_\lambda}(\theta_{12})I_m(\ell\varkappa+,\ \gamma_\lambda,\ \gamma_f)f_\ell^{(m,\varkappa_f)\epsilon_f}(r)=0 \tag{4.1a}$$

$$\left[L_{\theta 12}+\frac{2m}{\hbar^2}\left(E-\frac{2}{r_{12}}\right)\right]f_\ell^{(m,\varkappa)-}(r)-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\left[\left\{\frac{\ell(\ell+1)-\varkappa^2}{2\sin^2\theta_{12}}+\frac{\varkappa^2}{4}+\frac{\cot\theta_{12}}{2\sin\theta_{12}}\delta_{1\varkappa}(1-2A_\varkappa^\ell)\right\}f_\ell^{(m,\varkappa)-}(r)\right.$$
$$+\frac{\cot\theta_{12}}{\sin\theta_{12}}(1-\delta_{2,\varkappa+2})(\varkappa+1)(\varkappa+2)B_{\ell,\varkappa+2}f_\ell^{(m,\varkappa+2)-}(r)+\frac{\cot\theta_{12}}{4\sin\theta_{12}}(1-\delta_{0,\varkappa-2})\frac{A_{\varkappa-2}^\ell A_{\varkappa-1}^\ell}{\beta_{\ell\varkappa}}f_\ell^{(m,\varkappa-2)-}(r)\Big]$$
$$+\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\left[-\varkappa\left(\frac{\cos\theta_{12}}{2\sin\left(\frac{\theta_{12}}{2}\right)}-\cot\theta_{12}-\frac{1}{2\sin\theta_{12}}\right)f_\ell^{(m,\varkappa)+}(r)+\varkappa\frac{\partial f_\ell^{(m,\varkappa)+}(r)}{\partial\theta_{12}}-\frac{\delta_{1\varkappa}(1-2A_\varkappa^\ell)}{2\sin\theta_{12}}f_\ell^{(m,\varkappa)+}(r)\right.$$
$$\left.-\frac{(1-\delta_{2,\varkappa+2})(\varkappa+1)(\varkappa+2)}{\sin\theta_{12}}B_{\ell,\varkappa+2}f_\ell^{(m,\varkappa+2)+}(r)+\frac{1}{4\sin\theta_{12}}\frac{(1+3\delta_{0,\varkappa-2})}{(1+\delta_{0,\varkappa-2}(\sqrt{2}-1))}\frac{A_{\varkappa-2}^\ell A_{\varkappa-1}^\ell}{\beta_{\ell\varkappa}}f_\ell^{(m,\varkappa-2)+}(r)\right]$$
$$+\frac{2m}{\hbar^2}4\pi\sum_{\gamma_f}\sum_{j=1}^{2}\sum_{\lambda_\gamma(\text{even})}^{\prime\prime}g_\lambda\left(\frac{1}{2}R_{AB},\ r_j\right)(1-2\delta_{2j}\delta_{\epsilon_\lambda -})\alpha_\lambda^{\mu\epsilon_\lambda}(\theta_{12})I_m(\ell\varkappa-,\ \gamma_\lambda,\ \gamma_f)f_\ell^{(m,\varkappa_f)\epsilon_f}(r)=0 \tag{4.1b}$$

The index γ in the above formulae represents the triple indices ℓ, $\varkappa$, ϵ. For example

$$\gamma_f=\ell_f,\ \varkappa_f,\ \epsilon_f \tag{4.2}$$

A summation with respect to this index means:

$$\sum_{\gamma_f}\equiv\sum_{\ell_f}\sum_{\varkappa_f}\sum_{\epsilon_f} \tag{4.3a}$$

and in particular

$$\sum_{\gamma_\lambda(\text{even})}^{\prime\prime}=\sum_{\lambda\,(\text{even})}^{\prime\prime}\sum_{\mu\,(\text{even})}^{\prime\prime}\sum_{\epsilon_\lambda}^{\prime\prime} \tag{4.3b}$$

ϵ is a symbol which can be + or −, so that a sum over ϵ consists of only these two terms.

Aside from these abbreviations, the radial equations have been written above in a fairly explicit

form (with a corresponding sacrifice of elegance). For an arbitrary ℓ the coupling is reasonably complicated although as we shall see in the next section for ℓ small the equations simplify greatly. The nature of the coupling is nevertheless contained in the equations themselves via the selection rules for the various coefficients. Regarding the effect of the kinetic energy coupling, a verbal description of the nature of that coupling is given in reference 7.

The equations in the form given here are appropriate to the radial coordinates r_1, r_2, θ_{12} with

$$L_{\theta_{12}}=\frac{1}{r_1}\frac{\partial^2}{\partial r_1{}^2}r_1+\frac{1}{r_2}\frac{\partial^2}{\partial r_2{}^2}r_2 +\left(\frac{1}{r_1{}^2}+\frac{1}{r_2{}^2}\right)\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\left(\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right) \tag{4.4}$$

Also the fact that one has two functions (and hence two equations) for a given ℓ and $\varkappa$ indicates that the functions are in symmetric form. Hence the solutions may be confined to the region, say, $r_1>r_2$ with the boundary condition

$$\left[\frac{\partial f_\ell^{(m,\varkappa)\epsilon_1}}{\partial\eta}\right]_{r_1=r_2}=0 \tag{4.5a}$$

and

$$[f_\ell^{(m,\varkappa)\epsilon_2}]_{r_1=r_2}=0 \tag{4.5b}$$

where $\partial/\partial n$ is the normal derivative and ϵ_1 and ϵ_2 are the two choices of $+$ and $-$, being so selected according to (3.15) to give either the space symmetric (singlet) or the space antisymmetric (triplet) solution of the Schrödinger equation.

The coupling due to the potential energy is given in the last term of each of the radial equations. It can be seen that it alone is m dependent, and coupling coefficients I_m are:

$$I_m(\gamma,\gamma_\lambda,\gamma_{\ell'})=\frac{4\pi}{(2\lambda+1)^{\frac{1}{2}}}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}(D_\ell^{(m,\varkappa)\epsilon})^*D_\lambda^{(0,\mu)\epsilon_\lambda}D_{\ell'}^{(m,\varkappa')\epsilon'}\sin\theta d\theta d\Phi d\psi \tag{4.6a}$$

This quadrature, which is a linear combination of integrals of the form (3.11), yields:

$$I_m(\gamma,\gamma_\lambda,\gamma_{\ell'})=\frac{[(1+\delta_{0m}\delta_{0\varkappa}(\sqrt{2}-1))(1+\delta_{0\mu}(\sqrt{2}-1))(1+\delta_{0m}\delta_{0\varkappa'}(\sqrt{2}-1))]^{-1}}{\{\epsilon\}^*\{\epsilon_\lambda\}\{\epsilon_{\ell'}\}}$$
$$\sqrt{\frac{2(2\ell+1)}{(2\ell'+1)}}(1+\epsilon\epsilon_\lambda\epsilon_{\ell'}(-1)^{\ell+\ell'})(\ell\lambda-m0|\ell'\varkappa')[(\ell\lambda-\varkappa\mu|\ell'-\varkappa')+\epsilon_{\ell'}(\ell\lambda-\varkappa\mu|\ell'\varkappa')$$
$$+\epsilon_\lambda(\ell\lambda-\varkappa-\mu|\ell'-\varkappa')+\epsilon(\ell\lambda\varkappa\mu|\ell'-\varkappa')] \tag{4.6b}$$

Here the ϵ's are to be thought as the numbers ±1, and

$$\{\epsilon_\sigma\}=\{(1+\epsilon_\sigma)^{\frac{1}{2}}+i(1-\epsilon_\sigma)^{\frac{1}{2}}\} \tag{4.7}$$

These coefficients are subject to many restrictions if they are not to vanish. Also only one of the C-G coefficients in the final square bracket will not vanish when any of these indices are non-zero. (When $\varkappa=\mu=0$ all four terms contribute.)

V. TRUNCATION AND THE Σ_g^+ STATE OF H_2

The coupling in ℓ' and λ contained in the potential terms in principle includes a doubly infinite sum. If one truncates the sum in ℓ' at $\ell'=L$, then only a finite number of terms in the λ sum survive. The inclusion of all λ terms for a given L, then constitutes a given order of approximation in the context of the partial wave theory.

It is now our assertion that the solutions of successive approximation converges usefully. By this we mean two things; first that for a given L the $f_\ell'r)^{(m,\varkappa)\epsilon}$ from $\ell=\ell_i$ to $\ell=L$ get smaller in some sense. Secondly in going from one L to the next the $f_\ell(r)^{(m,\varkappa)\epsilon}$ for a given set of indices $(\ell,\varkappa,\epsilon)$ does not change much.

In view of the complicated nature of these equations this would be a very difficult thing to prove rigorously. The heuristic argument, however, follows that for the one-electron diatomic molecule[1]. Namely, in the centrifugal terms, which are those multiplied by $(r_1^{-2}+r_2^{-2})$ in the above

equations, there is a repulsive term proportional to $\ell(\ell+1)$ which tends to diminish the amplitude of each succeeding $f_\ell(r)$ component in the region of interaction.

Since, however, there are considerably more terms than this $\ell(\ell+1)$ term, the cogency of this argument is considerably more obscure than its one-electron counterpart[1] and in any event it is known from at least one atomic example that there can be resonance regions in which an additional ℓ component can in fact dominate its predecessors.[12]

We shall therefore examine one case in which there exist numerical results. Consider the Σ_g^+ states of H_2. In zeroth order ($L=0$) these states which include the ground state, are governed by the equation ($z=1$):

$$\left[\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1+\frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2+\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\left(\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right)+\frac{2m}{\hbar^2}\left(E-2/r_{12}+4g_0\left(\frac{1}{2}R_{AB},r_1\right)+4g_0\left(\frac{1}{2}R_{AB},r_2\right)\right)\right]f(r_1,\,r_2,\,\theta_{12})=0 \quad (5.1)$$

This is a three-dimensional partial differential equation for a single function ($f\equiv f_0^{(0,0)+}$). The expression in square brackets is manifestly invariant with respect to exchange, $r_1\rightleftarrows r_2$, and the singlet and triplet solutions are distinguished by the boundary conditions:

$$\left[\frac{\partial}{\partial n}f(r_1,\,r_2,\,\theta_{12})\right]_{r_1=r_2}=0 \qquad \text{singlet} \quad (5.2a)$$

$$[f(r_1,\,r_2,\,\theta_{12}]_{r_1=r_2}=0 \qquad \text{triplet} \quad (5.2b)$$

Below we shall outline a systematic approximation procedure for solving this equation. For completeness, however, we shall give this equation with r_1, r_2, and r_{12} as the independent variables:

$$\left[\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1+\frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2+\frac{2}{r_{12}}\frac{\partial^2}{\partial r_{12}^2}r_{12}+\frac{r_1^2+r_{12}^2-r_2^2}{r_1r_2}\frac{\partial^2}{\partial r_1\partial r_{12}}+\frac{r_2^2+r_{12}^2-r_1^2}{r_1r_2}\frac{\partial^2}{\partial r_2\partial r_{12}}+\frac{2m}{\hbar^2}\left(E-2|r_{12}+2g_0\left(\frac{1}{2}R_{AB},r_1\right)+2g_0\left(\frac{1}{2}R_{AB},r_2\right)\right)\right]f(r_1,\,r_2,\,\theta_{12})=0 \quad (5.3)$$

This form of the zeroth order equation is appropriate for solution in terms of Hylleraas-type expansions. In reference 7 other ways of writing these equations are given, involving in particular asymmetric functions $F\left(r_1,\,r_2,\begin{Bmatrix}\theta_{12}\\ r_{12}\end{Bmatrix}\right)$.

A methodical way of solving the θ_{12} equation is to make a *relative* partial wave expansion of f:

$$f(r_1,\,r_2,\,\theta_{12})=\sum_{n=0}^{\infty}\frac{1}{r_1r_2}\Phi_n(r_1r_2)P_n(\theta_{12}) \quad (5.4)$$

The Legendre polynomials $P_n(\theta_{12})$ are selected because they are the eigenfunctions of the θ_{12} derivative term in (5.1). Also the interelectron repulsion $1/r_{12}$ has a well known expansion in terms of $P_n(\theta_{12})$, so that one can easily derive an infinite set of two dimensional partial differential equation, which are essentially those that already have been derived in the case of the scattering of electrons from atomic hydrogen[13]. One can then truncate the sum at $n=N$ and expect convergence in N in a completely analogously way as one expects convergence in L in the partial wave theory as a whole.

Alternatively one can expand the total wave function in the form (considering here only the singlet case):

$$\Psi(1,2)=\sum_{n_1n_2}\sum_{\nu_1\nu_2}\sum_{\mu}C_{n_1n_2\nu_1\nu_2\mu}[R_{n_1\nu_1}(r_1)r_2^{\nu_2}\cdots)Y_{\nu_1\mu}^{n}(\Omega_1)Y_{\nu_2\mu}(\Omega_2)+(1\rightleftarrows 2)] \quad (5.5)$$

If one restricts this sum to $\nu_1=\nu_2$ and all values of μ for each ν_1, then this expansion is equivalent

to (5.4). A detailed investigation of the ground Σ_g^+ state of H_2 using (5.5) has been carried out by Hagstrum and Shull[14]. They have in fact relaxed the condition $\nu_1 = \nu_2$, so that what they approximate in those cases is a hybrid of approximations within the partial wave theory. They have, however, examined the $\nu_1 = \nu_2 = 0$ (spherically averaged) approximation. This is equivalent to including one term in (5.4) within the $L = 0$ (zeroth order) approximation. They obtain $E = -2.0894$ ryd. (1 ryd. = 13.6 eV) at $R_{AB} = 1.4$ Bohr radius. It is quite clear that the inclusion of all $\nu_1 = \nu_2$ and with their associated μ terms will lower this energy to below -2.1 ryd. Such a value is to be compared to $E = -2.34\ 884$ ryd., the very accurate nonrelativistic value (including the nuclear repulsion) of Kolos and Roothan[15]. The differences between these numbers, less than 0.2 ryd., is very close to the difference between the zeroth order and exact H_2^+ energies near their minimum ($R_{AB} = 2$)[1]. This is just what our heuristic argument would lead us to expect in view of the fact, this being a Σ state, that the next angular momentum, $\ell = 2$, is two units greater than the included $\ell = 0$ component of the zeroth order problem, in complete analogy with the case for the H_2^+ molecular ion[1]. In addition for the exact solutions of the partial wave approximations the analogy carries through regarding the upper boundedness of the energies of the ground and excited state solutions and of their mutual orthogonality[1].

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