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DECOMPOSITION OF THE SCHRÖDINGER EQUATION FOR TWO IDENTICAL PARTICLES AND A THIRD PARTICLE OF FINITE MASS

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Decomposition of the Schrödinger Equation for Two Identical Particles and a Third Particle of Finite Mass

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An angular momentum decomposition of the Schrödinger equation is extended to the case noted in the title. (The case of three unequal mass particles is treated in an appendix.) The decomposition is effected with the use of a symmetric choice of Euler angles, and the radial equations are given in two useful forms. The radial equations are shown to yield the Born-Oppenheimer equations for H_2^+ in the limit that the two identical particles approach infinite mass. Other aspects of this limit are discussed, and general rules which relate the total angular momentum states of the three-body system with the molecular states of H_2^+ are examined.

Author

I INTRODUCTION

In a previous review[1] we have presented a detailed investigation of the decomposition of the Schrödinger equation for two identical particles, obeying the exclusion principle, in the central field of an infinitely heavy center of force. This, of course, is the prototype of the two-electron atom. The major correction to this idealization is the recoil effects of the nucleus. It is the primary purpose of this paper ti give the extension of the above decomposition to include the finite mass of the previously assumed fixed center. (The changes necessary in the radial equations for three unequal mass particles are given in Appendix B.)

The resulting decomposition is still sufficiently general to allow an arbitrary mass to the identical particles as well as the nonidentical third particle. As a rather different limit of this system from the previous one, one can consider the limit in which the two identical particles become infinitely heavy and the third particle assumes the electron mass. This corresponds to the H_2^+ limit, and it is of considerable interest to see how the radial equations and the three-body symmetries go over into the equations and symmetries of the Born-Oppenheimer approximation in that case.

This is particularly relevant at the present time since the absorption of μ mesons in hydrogen[2] via the molecule ($p - \mu - p$) can presumably only be explained by the deviations of this μ mesic counterpart of H_2^+ from the Born-Oppenheimer approximation[3]. The H_2^+ limit will be the subject of Section III.

II KINETIC ENERGY AND RADIAL EQUATIONS

Let $\underset{\sim}{\rho}_1$ and $\underset{\sim}{\rho}_2$ be the coordinates of two identical particles, each of mass m, in an arbitrary fixed coordinate system. Let $\underset{\sim}{\rho}_3$ be the coordinates of a third particle of mass M. The kinetic energy can be written:

$$T = -\frac{1}{2m}\left(\nabla_{\rho_1}^2 + \nabla_{\rho_2}^2\right) - \frac{1}{2M}\nabla_{\rho_3}^2 \tag{2.1}$$

With the introduction of the difference vectors

$$\underset{\sim}{r}_1 = \underset{\sim}{\rho}_1 - \underset{\sim}{\rho}_3 \tag{2.2a}$$

$$\underset{\sim}{r}_2 = \underset{\sim}{\rho}_2 - \underset{\sim}{\rho}_3 \tag{2.2b}$$

and the center of mass coordinate $\underset{\sim}{R}$:

$$\underset{\sim}{R} = \frac{m(\underset{\sim}{\rho}_1 + \underset{\sim}{\rho}_2) + M\underset{\sim}{\rho}_3}{2m + M} \tag{2.2c}$$

the kinetic energy becomes

$$T = -\frac{1}{2\mu}\left(\nabla_{r_1}^2 + \nabla_{r_2}^2\right) - \frac{1}{M}\,\nabla_{\underset{\sim}{r_1}}\cdot\nabla_{\underset{\sim}{r_2}} - \frac{1}{2(2m+M)}\,\nabla_R^2, \tag{2.3a}$$

where

$$\mu = \frac{mM}{m+M}. \tag{2.4}$$

The last term in (2.3a) is clearly the kinetic energy of the center of mass. In any closed system the potential will be independent of $\underset{\sim}{R}$, so that the effect of this term will be to subtract a center of mass energy, E_{CM}, from the total energy, E_T, to give an effective energy E for a Schrödinger equation with the last term in (2.3a) absent. Thus we can replace the kinetic energy by an effective kinetic energy governing the internal motion

$$T_e = -\frac{1}{2\mu}\left(\nabla_{r_1}^2 + \nabla_{r_2}^2\right) - \frac{1}{M}\,\nabla_{\underset{\sim}{r_1}}\cdot\nabla_{\underset{\sim}{r_2}}, \tag{2.3b}$$

to be used with an effective energy

$$E = E_T - E_{CM} \tag{2.5}$$

T_e now differs in form from the kinetic energy of the two-electron fixed nucleus problem[1] by the addition of the final cross term. This additional term is the well-known mass polarization term which in most helium applications is treated in perturbation theory (which is quite adequate for the present experimental accuracy).[4] We shall include the effect of this term exactly.

It will be recalled from I that the major task in effecting the decomposition is to find the kinetic energy in terms of the Euler angles and residual coordinates in place of the particle coordinates. We introduce formally the same Euler angles as in I; namely Θ the angle between the space-fixed $\hat{z}$ direction and $\hat{r}_1 \times \hat{r}_2 \sim \hat{z}'$, Φ the angle between the space-fixed $\hat{x}$ direction, and $\hat{z} \times \hat{z}' \sim \hat{x}'$, and Ψ the angle between $\hat{x}'$ and $(\hat{r}_2 - \hat{r}_1)$. Now, since the form of $\nabla^2_{r_1} + \nabla^2_{r_2}$ is the same as in I, the transformation of those terms in terms of the three Euler angles and three residual coordinates can simply be taken over from I. We need only consider therefore the remaining cross term, and since we handle it in a very similar manner, we shall be mercifully brief.

In spherical coordinates the cross term is

$$\underset{\sim}{\nabla}_{r_1} \cdot \underset{\sim}{\nabla}_{r_2} = \cos\theta_{12} \frac{\partial^2}{\partial r_1 \partial r_2} + \left\{ \frac{1}{r_1} \left(u \frac{\partial^2}{\partial r_2 \partial \vartheta_1} + v \frac{\partial^2}{\partial r_2 \partial \varphi_1} \right) + (1 \rightleftarrows 2) \right\}$$

$$+ \frac{1}{r_1 r_2} \left\{ a \frac{\partial^2}{\partial\vartheta_1 \partial\vartheta_2} + b \frac{\partial^2}{\partial\varphi_1 \partial\varphi_2} + \left[c \frac{\partial^2}{\partial\vartheta_1 \partial\varphi_2} + (1 \rightleftarrows 2) \right] \right\} \tag{2.6}$$

where

$$u = \sin\vartheta_2 \cos\vartheta_1 \cos(\varphi_2 - \varphi_1) - \cos\vartheta_2 \sin\vartheta_1 \tag{2.7}$$

$$v = \frac{\sin\vartheta_2}{\sin\vartheta_1} \sin(\varphi_2 - \varphi_1) \tag{2.8}$$

$$a = \cos\vartheta_1 \cos\vartheta_2 \cos(\varphi_2 - \varphi_1) + \sin\vartheta_1 \sin\vartheta_2 \tag{2.9}$$

$$b = \frac{\cos(\varphi_2 - \varphi_1)}{\sin\vartheta_1 \sin\vartheta_2} \tag{2.10}$$

$$c = \frac{\cos\vartheta_1 \sin(\varphi_1 - \varphi_2)}{\sin\vartheta_2} \tag{2.11}$$

When the residual coordinates are taken as r_1, r_2, Θ_{12}, then the transformation only involves first and second partial derivatives of $\vartheta_1, \varphi_1, \vartheta_2, \varphi_2$ with respect to $\Theta, \Phi, \Psi, \Theta_{12}$. (The latter are referred to as χ_α, $\alpha = 1 \ldots 4$ below). The cross term can therefore be written

$$\begin{aligned}
\nabla_{r_1} \cdot \nabla_{r_2} = {} & \cos\Theta_{12} \frac{\partial^2}{\partial r_1 \partial r_2} + \sum_{\alpha=1}^{4} \Big[\frac{1}{r_1} \Big(u \frac{\partial \chi_\alpha}{\partial \vartheta_1} + v \frac{\partial \chi_\alpha}{\partial \varphi_1} \Big) \frac{\partial^2}{\partial \chi_\alpha \partial r_2} \\
& + (1 \rightleftarrows 2) \Big] + \frac{1}{r_1 r_2} \Big\{ \sum_{\alpha=1}^{4} \Big[a \frac{\partial \chi_\alpha}{\partial \vartheta_1} \frac{\partial \chi_\alpha}{\partial \vartheta_2} + b \frac{\partial \chi_\alpha}{\partial \varphi_1} \frac{\partial \chi_\alpha}{\partial \varphi_2} \\
& + \Big(c \frac{\partial \chi_\alpha}{\partial \vartheta_1} \frac{\partial \chi_\alpha}{\partial \varphi_2} + 1 \rightleftarrows 2 \Big) \Big] \frac{\partial^2}{\partial \chi_\alpha^2} + \sum_{\alpha=1}^{4} \Big[a \frac{\partial^2 \chi_\alpha}{\partial \vartheta_1 \partial \vartheta_2} \\
& + b \frac{\partial^2 \chi_\alpha}{\partial \varphi_1 \partial \varphi_2} + \Big(c \frac{\partial^2 \chi_\alpha}{\partial \vartheta_1 \partial \varphi_2} + (1 \rightleftarrows 2) \Big) \Big] \frac{\partial}{\partial \chi_\alpha} \\
& + \sum_{\alpha} \sum_{> \beta = 1}^{4} \Big[a \Big\{ \frac{\partial \chi_\alpha}{\partial \vartheta_1} \frac{\partial \chi_\beta}{\partial \vartheta_2} + (1 \rightleftarrows 2) \Big\} + b \Big\{ \frac{\partial \chi_\alpha}{\partial \varphi_1} \frac{\partial \chi_\beta}{\partial \varphi_2} \\
& + (1 \rightleftarrows 2) \Big\} + \Big\{ c \Big(\frac{\partial \chi_\alpha}{\partial \vartheta_1} \frac{\partial \chi_\beta}{\partial \varphi_2} + \frac{\partial \chi_\alpha}{\partial \varphi_2} \frac{\partial \chi_\beta}{\partial \vartheta_1} \Big) + (1 \rightleftarrows 2) \Big\} \Big] \frac{\partial^2}{\partial \chi_\alpha \partial \chi_\beta}
\end{aligned} \tag{2.12}$$

The results in the form of the coefficients of the derivatives with respect to X_α expressed as functions of θ, Φ, ψ, θ_{12} are given in Table I. Finally we can write the cross term as an operator whose effect on the vector spherical harmonics have been fully explored in I.

$$
\begin{aligned}
\nabla_{r_1} \cdot \nabla_{r_2} = {} & \cos\theta_{12} \frac{\partial^2}{\partial r_1 \partial r_2} - \frac{\sin\theta_{12}}{r_2} \frac{\partial}{\partial r_1} \left(\frac{\partial}{\partial \theta_{12}} + \frac{1}{2} \frac{\partial}{\partial \psi} \right) \\
& - \frac{\sin\theta_{12}}{r_1} \frac{\partial}{\partial r_2} \left(\frac{\partial}{\partial \theta_{12}} - \frac{1}{2} \frac{\partial}{\partial \psi} \right) \\
& + \frac{1}{r_1 r_2} \Big[- \frac{1}{\sin\theta_{12}} \frac{\partial}{\partial \theta_{12}} - \cos\theta_{12} \frac{\partial^2}{\partial \theta_{12}^2} + \frac{\cos\theta_{12}}{4} \frac{\partial^2}{\partial \psi^2} \\
& - \frac{1}{2\sin^2\theta_{12}} \left(\sin 2\psi \, \Lambda_2 - \cos 2\psi \, \Lambda_1 \right) \\
& + \frac{\cos\theta_{12}}{2\sin^2\theta_{12}} \left(\frac{\partial^2}{\partial \psi^2} + \frac{M^2}{\hbar^2} \right) \Big]
\end{aligned}
\qquad (2.13)
$$

Λ_1 and Λ_2 are given in (I64) and M^2 is the well-known total angular momentum squared operator, (I41), in terms of the Euler angles.

The wave function is now expanded in the form (I55)

$$\underset{\sim}{\Psi}_{\ell m}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = \sum_{\varkappa}{}'' \Big[f_\ell^{\varkappa +}(r_1, r_2, \theta_{12})\, \mathcal{D}_\ell^{(m,\varkappa)+}(\theta, \Phi, \Psi) + f_\ell^{\varkappa -}(r_1, r_2, \theta_{12})\, \mathcal{D}_\ell^{(m,\varkappa)-}(\theta, \Phi, \Psi) \Big] \tag{2.14}$$

where $\mathcal{D}_\ell^{(m,\varkappa)\pm}$ are the exchange vector spherical harmonics (I54), the simultaneous eigenfunctions of $\underset{\sim}{M}^2$, M_z and $\mathcal{E}_{12}$. The operator $\underset{\sim}{\nabla}_{r_1} \cdot \underset{\sim}{\nabla}_{r_2}$ as expressed (2.13) is now such that its operation on these $\mathcal{D}_\ell^{(m,\varkappa)\pm}$ functions can readily be found from (I65,66). Thus the radial equations can simply be derived as an addition of terms to what was derived in I. Below we shall give the equations in two forms; the first in terms of simultaneous coupled equations for the "radial" functions $f_\ell^{\varkappa\pm}(r_1, r_2, \theta_{12})$:

$$\Big[L_{\theta_{12}} + \frac{2\mu}{\hbar^2}(E - V)\Big] f_\ell^{\varkappa +} - \Big(\frac{1}{r_1^2} + \frac{1}{r_2^2}\Big)\Big[\Big\{ \frac{\ell(\ell+1) - \varkappa^2}{2\sin^2\theta_{12}} + \frac{\varkappa^2}{4}$$

$$- \frac{\cot\theta_{12}}{4\sin\theta_{12}}\, \ell(\ell+1)\,\delta_{1\varkappa}\Big\} f_\ell^{\varkappa +} + \frac{\cot\theta_{12}}{4\sin\theta_{12}}\Big\{ B_\ell^{\varkappa+2} f_\ell^{(\varkappa+2)+} + (1 - \delta_{0\varkappa} - \delta_{1\varkappa} + \delta_{2\varkappa}) B_{\ell\varkappa} f_\ell^{(\varkappa-2)+}\Big\}\Big]$$

$$+ \Big(\frac{1}{r_1^2} - \frac{1}{r_2^2}\Big)\Big[- \Big\{ \varkappa\Big(\frac{1}{2}\cot\theta_{12} + \frac{\partial}{\partial\theta_{12}}\Big) + \frac{\ell(\ell+1)\,\delta_{1\varkappa}}{4\sin\theta_{12}} \Big\} f_\ell^{\varkappa -}$$

$$+ \frac{1}{4\sin\theta_{12}}\Big\{ B_\ell^{\varkappa+2} f_\ell^{(\varkappa+2)-} - (1 - \delta_{0\varkappa} - \delta_{1\varkappa} - \delta_{2\varkappa}) B_{\ell\varkappa} f_\ell^{(\varkappa-2)-} \Big\}\Big]$$

$$+ \frac{2\mu}{M}\frac{1}{r_1 r_2}\Big[\Big\{ \frac{\cos\theta_{12}}{2\sin^2\theta_{12}}\big(\ell(\ell+1) - \varkappa^2\big) - \frac{\varkappa^2}{4}\cos\theta_{12} - \frac{\ell(\ell+1)}{4\sin^2\theta_{12}}\,\delta_{1\varkappa}\Big\} f_\ell^{\varkappa +}$$

$$+ \frac{1}{4\sin^2\theta_{12}} \left\{ B_\ell^{\kappa+2} f_\ell^{(\kappa+2)+} + (1-\delta_{0\kappa}-\delta_{1\kappa}+\delta_{2\kappa}) B_{\ell\kappa} f_\ell^{(\kappa-2)+} \right\} \Big]$$

$$+ \frac{2\mu}{M} \Big[\Big\{ \cos\theta_{12} \frac{\partial^2}{\partial r_1 \partial r_2} - \frac{\sin\theta_{12}}{r_2} \frac{\partial^2}{\partial r_1 \partial\theta_{12}} - \frac{\sin\theta_{12}}{r_1} \frac{\partial^2}{\partial r_2 \partial\theta_{12}} - \frac{1}{r_1 r_2 \sin\theta_{12}} \frac{\partial}{\partial\theta_{12}}$$

$$- \frac{\cos\theta_{12}}{r_1 r_2} \frac{\partial^2}{\partial\theta_{12}^2} \Big\} f_\ell^{\kappa+} + \frac{\kappa}{2} \sin\theta_{12} \left(\frac{1}{r_1}\frac{\partial}{\partial r_2} - \frac{1}{r_2}\frac{\partial}{\partial r_1} \right) f_\ell^{\kappa-} \Big] = 0$$

(2.15a)

$$\Big[L_{\theta_{12}} + \frac{2\mu}{\hbar^2}(E-V) \Big] f_\ell^{\kappa-} - \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \Big[\Big\{ \frac{\ell(\ell+1)-\kappa^2}{2\sin^2\theta_{12}} + \frac{\kappa^2}{4} + \frac{\cot\theta_{12}}{4\sin\theta_{12}} \ell(\ell+1)\delta_{1\kappa} \Big\} f_\ell^{\kappa-}$$

$$+ \frac{\cot\theta_{12}}{4\sin\theta_{12}} \left\{ (1-\delta_{0\kappa}) B_\ell^{\kappa+2} f_\ell^{(\kappa+2)-} + (1-\delta_{0\kappa}-\delta_{1\kappa}-\delta_{2\kappa}) B_{\ell\kappa} f_\ell^{(\kappa-2)-} \right\} \Big]$$

$$+ \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \Big[\Big\{ \kappa \left(\frac{1}{2}\cot\theta_{12} + \frac{\partial}{\partial\theta_{12}} \right) - \frac{\ell(\ell+1)}{4\sin\theta_{12}} \delta_{1\kappa} \Big\} f_\ell^{\kappa+}$$

$$- \frac{1}{4\sin\theta_{12}} \left\{ (1-\delta_{0\kappa}) B_\ell^{\kappa+2} f_\ell^{(\kappa+2)+} - (1-\delta_{0\kappa}-\delta_{1\kappa}+\delta_{2\kappa}) B_{\ell\kappa} f_\ell^{(\kappa-2)+} \right\} \Big]$$

$$+ \frac{2\mu}{M} \frac{1}{r_1 r_2} \Big[\Big\{ \frac{\cos\theta_{12}}{2\sin^2\theta_{12}} (\ell(\ell+1)-\kappa^2) - \frac{\kappa^2}{4}\cos\theta_{12} + \frac{\ell(\ell+1)\delta_{1\kappa}}{4\sin^2\theta_{12}} \Big\} f_\ell^{\kappa-}$$

$$+ \frac{1}{4\sin^2\theta_{12}} \left\{ (1-\delta_{0\kappa}) B_\ell^{\kappa+2} f_\ell^{(\kappa+2)-} + (1-\delta_{0\kappa}-\delta_{1\kappa}-\delta_{2\kappa}) B_{\ell\kappa} f_\ell^{(\kappa-2)-} \right\} \Big]$$

$$+ \frac{2\mu}{M} \Big[\Big\{ \cos\theta_{12} \frac{\partial^2}{\partial r_1 \partial r_2} - \frac{\sin\theta_{12}}{r_2} \frac{\partial^2}{\partial r_1 \partial\theta_{12}} - \frac{\sin\theta_{12}}{r_1} \frac{\partial^2}{\partial r_2 \partial\theta_{12}} - \frac{1}{r_1 r_2 \sin\theta_{12}} \frac{\partial}{\partial\theta_{12}}$$

$$- \frac{\cos\theta_{12}}{r_1 r_2} \frac{\partial^2}{\partial\theta_{12}^2} \Big\} f_\ell^{\kappa-} + \frac{\kappa}{2} \sin\theta_{12} \left(\frac{1}{r_2}\frac{\partial}{\partial r_1} - \frac{1}{r_1}\frac{\partial}{\partial r_2} \right) f_\ell^{\kappa+} \Big] = 0$$

(2.15b)

The numbers $B_{\ell\varkappa}$ and $B_\ell^\varkappa$ are defined in (I68), and S-wave operator $L_{\theta_{12}}$ in (I71). The fact that the equations are in this first form are coupled for a given $\varkappa$ implies that we are dealing with symmetric and antisymmetric functions

$$f_\ell^{\varkappa +}(r_1, r_2, \theta_{12}) = \pm (-1)^{\ell+\varkappa} f_\ell^{\varkappa +}(r_2, r_1, \theta_{12}) \tag{2.16a}$$

$$f_\ell^{\varkappa -}(r_1, r_2, \theta_{12}) = \pm (-1)^{\ell+\varkappa+1} f_\ell^{\varkappa -}(r_2, r_1, \theta_{12}) \tag{2.16b}$$

where the upper sign refers to the totally space symmetric wave function (singlet) and the lower to the space antisymmetric solution (triplet). The (anti) symmetry means that we can confine the solution to half the r_1 - r_2 plane with an appropriate vanishing of the function or its normal derivative along $r_1 = r_2$ (cf. Eqs. (I72) and (I73)).

The second form of these equations that we shall give involves the "radial" coordinates r_1, r_2, r_{12} and involves the asymmetric functions $F_\ell^\varkappa$ and $\tilde{F}_\ell^\varkappa$.

$$F_\ell^\varkappa(r_1, r_2, r_{12}) = f_\ell^{\varkappa +}(r_1, r_2, \theta_{12}) + f_\ell^{\varkappa -}(r_1, r_2, \theta_{12}) \tag{2.17a}$$

$$\tilde{F}_\ell^{\varkappa}(r_1, r_2, r_{12}) = f_\ell^{\varkappa +}(r_1, r_2, \theta_{12}) - f_\ell^{\varkappa -}(r_1, r_2, \theta_{12}) \tag{2.17b}$$

where, on the rhs, Θ_{12} is understood to be expressed as a function of r_1, r_2, r_{12} through the law of cosines. By virtue of (2.16) we have

$$\tilde{F}_\ell^{\varkappa}(r_2, r_1, r_{12}) = \pm (-1)^{\ell + \varkappa} F_\ell^{\varkappa}(r_1, r_2, r_{12}). \tag{2.18}$$

This relation enables us to write the equations in an uncoupled form for a given $\varkappa$ (the various $\varkappa$'s are of course coupled to each other) but in a domain covering the whole $r_2 - r_1$ plane. It is also convenient in writing this second form to combine some of the terms multiplied by $2\,\mu/M$ in (2.15) with $L_{r_{12}}$ (given in (I81)) to form a new S-wave operator $L'_{r_{12}}$:

$$\begin{aligned} L'_{r_{12}} = {} & \frac{1}{r_1}\frac{\partial^2}{\partial r_1^2} r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2} r_2 + \frac{\mu}{m}\Big[\frac{2}{r_{12}}\frac{\partial^2}{\partial r_{12}^2} r_{12} \\ & + \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}} \Big] + \frac{\mu}{M}\frac{r_1^2 + r_2^2 - r_{12}^2}{r_1 r_2}\frac{\partial^2}{\partial r_1 \partial r_2} \end{aligned} \tag{2.19}$$

We also use the quantity ρ

$$\rho = \left[-r_{12}^4 - (r_1^2 - r_2^2)^2 + 2 r_{12}^2 (r_1^2 + r_2^2) \right]^{\frac{1}{2}} \tag{2.20}$$

The equations are:

$$\Big[L'_{r_{12}} + \frac{2\mu}{\hbar^2}(E - V) \Big] F_\ell^{\varkappa} - \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) \Big[\Big\{ (\ell(\ell+1) - \varkappa^2) \frac{2 r_1^2 r_2^2}{\rho^2} + \frac{\varkappa^2}{4} \Big\} F_\ell^{\varkappa}$$

$$- \ell(\ell+1)(r_1^2 + r_2^2 - r_{12}^2) \frac{r_1 r_2}{2\rho^2} \delta_{1\varkappa} \tilde{F}_\ell^{\varkappa} + B_\ell^{\varkappa+2} (r_1^2 + r_2^2 - r_{12}^2) \frac{r_1 r_2}{2\rho^2} \Big\{ F_\ell^{\varkappa+2}$$

$$- \frac{\delta_{0\varkappa}}{2} (F_\ell^{\varkappa+2} - \tilde{F}_\ell^{\varkappa+2}) \Big\} + B_{\ell\varkappa} (r_1^2 + r_2^2 - r_{12}^2) \frac{r_1 r_2}{2\rho^2} (1 - \delta_{0\varkappa} - \delta_{1\varkappa}) \Big\{ F_\ell^{\varkappa-2}$$

$$+ \delta_{2\varkappa} \tilde{F}_\ell^{\varkappa-2} \Big\} \Big] + \left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right) \Big[\frac{\varkappa}{2} \Big\{ \frac{r_1^2 + r_2^2 - r_{12}^2}{\rho}$$

$$+ \frac{\mu}{m} \frac{\rho}{r_{12}} \frac{\partial}{\partial r_{12}} \Big\} \tilde{F}_\ell^{\varkappa} - \frac{\ell(\ell+1)}{2} \frac{r_1 r_2}{\rho} \delta_{1\varkappa} F_\ell^{\varkappa} + B_\ell^{\varkappa+2} \frac{r_1 r_2}{2\rho} \Big\{ - \tilde{F}_\ell^{\varkappa+2}$$

$$+ \frac{\delta_{0\varkappa}}{2} (F_\ell^{\varkappa+2} + \tilde{F}_\ell^{\varkappa+2}) \Big\} + B_{\ell\varkappa} \frac{r_1 r_2}{2\rho} (1 - \delta_{0\varkappa} - \delta_{1\varkappa}) \Big\{ \tilde{F}_\ell^{\varkappa-2} + \delta_{2\varkappa} F_\ell^{\varkappa-2} \Big\} \Big]$$

$$+ \frac{2\mu}{M} \Big[(r_1^2 + r_2^2 - r_{12}^2) \Big\{ \frac{\ell(\ell+1) - \varkappa^2}{\rho^2} - \frac{\varkappa^2}{8 r_1^2 r_2^2} \Big\} F_\ell^{\varkappa}$$

$$- \ell(\ell+1) \frac{r_1 r_2}{\rho^2} \delta_{1\varkappa} \tilde{F}_\ell^{\varkappa} + \frac{\varkappa \rho}{4 r_1 r_2} \left(\frac{1}{r_2} \frac{\partial}{\partial r_1} - \frac{1}{r_1} \frac{\partial}{\partial r_2} \right) \tilde{F}_\ell^{\varkappa}$$

$$+ B_\ell^{\varkappa+2} \frac{r_1 r_2}{\rho^2} \Big\{ F_\ell^{\varkappa+2} - \frac{\delta_{0\varkappa}}{2} (F_\ell^{\varkappa+2} - \tilde{F}_\ell^{\varkappa+2}) \Big\} + B_{\ell\varkappa} \frac{r_1 r_2}{\rho^2} (1 - \delta_{0\varkappa} - \delta_{1\varkappa}) \Big\{ F_\ell^{\varkappa-2}$$

$$+ \delta_{2\varkappa} \tilde{F}_\ell^{\varkappa-2}) \Big\} \Big] = 0 \tag{2.21}$$

III THE H_2^+ LIMIT

Consider the limit in which the mass of the two identical particles becomes infinite and the third particle retains its finite mass. We shall call this the H_2^+ limit even though in a real H_2^+ molecular ion the two nuclei are not infinitely heavy and the system should be described by the complete equations we have given in the previous section. Mathematically this limit is defined by

$$m = M_p \to \infty \tag{3.1a}$$

$$M = m_e \tag{3.1b}$$

$$\lim_{M_p \to \infty} \mu = m_e \tag{3.1c}$$

The kinetic energy becomes

$$\lim_{M_p \to \infty} T_e = -\frac{\hbar^2}{2m_e} \left(\nabla_{r_1}^2 + \nabla_{r_2}^2 + 2\, \nabla_{r_1} \cdot \nabla_{r_2} \right) \tag{3.2}$$

Letting

$$\underset{\sim}{r} = -\frac{1}{2}(\underset{\sim}{r}_1 + \underset{\sim}{r}_2) \tag{3.3}$$

$$\underset{\sim}{r}_{12} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2, \tag{3.4}$$

From (3.3) $\underset{\sim}{r}$ is obviously the vector from the midpoint of the two nuclei to the electron; we find for the effective kinetic energy:

$$T_e = -\frac{\hbar^2}{2m_e}\nabla_r^2 \quad , \tag{3.5}$$

so that the Schrödinger equation becomes

$$\left[\nabla_r^2 + \frac{2m_e}{\hbar^2}(E - V)\right]\Psi = 0 \tag{3.6}$$

This is, of course, the Born-Oppenheimer approximation[5] for the electronic motion of H_2^+.

The potential V, being the attraction of the two nuclei considered as fixed centers to the electron, is not spherically symmetric. As a result the total angular momentum of the electron is not conserved but its z-component is (the z-axis being defined as the line joining the two nuclei). Appropriate solutions of (3.6) can therefore be written

$$\Psi = e^{i\Lambda\varphi} f_\Lambda(r, \vartheta), \tag{3.7}$$

where φ and ϑ are the polar angles of $\underset{\sim}{r}$ (the vector coordinate of the electron). Substitution of (3.7) into (3.6) yields

$$\left[\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2 \sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} - \frac{\Lambda^2}{r^2\sin^2\vartheta} + \frac{2m_e}{\hbar^2}(E - V)\right] f_\Lambda = 0, \tag{3.8a}$$

where $\Lambda = 0, 1, 2, \ldots$ correspond to the Σ, Π, Δ ... electronic states of H_2^+. The solutions can further be separated into even or odd electron parity ($\vartheta \to \pi - \vartheta$, $\varphi \to \pi + \varphi$) corresponding to <u>gerade</u> and <u>ungerade</u> classes.

Our purpose is to derive (3.8) from the radial equations of the three-body system in the H_2^+ limit. This provides not only a useful check of the radial equations themselves, but it allows for the verification of general rules which relate total angular momentum states of the three-body system to their Born-Oppenheimer counterparts as one-body systems in an axially symmetric field.

We shall do this in the following way: we shall actually show for the first couple of total ℓ radial equations in the H_2^+ limit that they reduce to the form (3.8) for specific values of Λ. This will enable us to adduce a general relationship between total ℓ - states and the Born-Oppenheimer electronic states that they correspond to. Then we shall derive a formula relating the parity of the molecular electronic state to the parity and exchange character of the three-body wave function.

A. $\ell = 0$

From (2.21) in the limit defined by (3.1) we have

$$\left[L'_{r_{12}} + \frac{2m_e}{\hbar^2}(E - V)\right]F_0^0 \tag{3.9}$$

where $L'_{r_{12}}$ is given in (2.19). The latter is seen to depend differentially only on two coordinate: r_1 and r_2. This is already the seed of the Born-Oppenheimer limit which will be seen to apply to all ℓ equations.

Letting $\eta = \left|\frac{1}{2}(\underline{r}_1 + \underline{r}_2)\right|$ $\xi = r_{12}$ and $\rho = r_1^2 - r_2^2$, we find

$$L'_{r_{12}} = \frac{2}{\eta}\frac{\partial}{\partial\eta} - \frac{\xi^2}{\rho^3}\frac{\partial}{\partial\rho} + \frac{\partial^2}{\partial\eta^2} + \frac{\rho}{\eta}\frac{\partial^2}{\partial\eta\,\partial\rho} + \frac{\xi^2}{\rho^2}\frac{\partial^2}{\partial\rho^2} \tag{3.10}$$

Now letting $r = \eta$, $\cos\vartheta = \underline{\xi}\cdot\underline{\eta}/\xi\eta = \frac{\xi^2}{2\xi r}$ we find further

$$L'_{r_{12}} = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} \tag{3.11}$$

Thus (3.9) reduces to (3.8) for $\Lambda = 0$. I.e. the $\ell = 0$ radial equation reduces to that for Σ states in the Born-Oppenheimer limit.

The difference between the Σ and higher Λ equations consists of terms proportional to $(r^2 \sin^2\vartheta)^{-1}$. We need only note the relation

$$4\frac{r_{12}^2}{\rho^2} = (r^2\sin^2\vartheta)^{-1} \tag{3.12}$$

so that the Born-Oppenheimer equations in general can be written

$$\left[L'_{r_{12}} - \Lambda^2 \frac{4 r_{12}^2}{\rho^2} + \frac{2me}{\hbar^2}(E - V) \right] f_\Lambda = 0 \tag{3.8b}$$

B. $\ell = 1$ even parity

For $\ell = 1$ and $\varkappa = 0$, Eq. (2.21) reduces to

$$\left[L'_{r_{12}} - \frac{4 r_{12}^2}{\rho^2} + \frac{2me}{\hbar^2}(E - V) \right] F_1^0 = 0 \tag{3.13}$$

Comparing with Eq. (3.8b) we see that this is the Born-Oppenheimer equation for Π states.

C. $\ell = 1$ odd parity

We get from Eq. (2.20) for $\ell = 1$, $\varkappa = 1$

$$\left[L'_{r_{12}} + \frac{2me}{\hbar^2}(E - V) \right] F_1^1 - \left[\frac{2 r_{12}^2}{\rho^2} + \frac{2 r_1^2 + 2 r_2^2 - r_{12}^2}{4 r_1^2 r_2^2} - \frac{r_1^2 - r_2^2}{r_1 r_2 \rho} \right] F_1^1$$

$$+ \left[\frac{(r_1^2 - r_2^2)^2 - r_{12}^2 (r_1^2 + r_2^2)}{r_1 r_2 \rho^2} + \frac{(r_2^2 - r_1^2)(r_1^2 + r_2^2 - r_{12}^2)}{2 r_1^2 r_2^2 \rho} \right.$$

$$\left. + \frac{\rho}{2 r_1 r_2} \left(\frac{1}{r_2} \frac{\partial}{\partial r_1} - \frac{1}{r_1} \frac{\partial}{\partial r_2} \right) \right] \tilde{F}_1^1 = 0 \tag{3.15a}$$

It is also convenient to derive a redundant equation. Letting $r_1 \rightleftarrows r_2$ in (3.15a) and using (2.18), we obtain

$$\left[L'_{r_{12}} + \frac{2m_e}{\hbar^2}(E-V) \right] \tilde{F}_1' - \left[\frac{2r_{12}^2}{\rho^2} + \frac{2r_1^2 + 2r_2^2 - r_{12}^2}{4r_1^2 r_2^2} + \frac{r_1^2 - r_2^2}{r_1 r_2 \rho} \right] \tilde{F}_1'$$

$$+ \left[\frac{(r_1^2 - r_2^2)^2 - r_{12}^2(r_1^2 + r_2^2)}{r_1 r_2 \rho^2} - \frac{(r_2^2 - r_1^2)(r_1^2 + r_2^2 - r_{12}^2)}{2r_1^2 r_2^2 \rho} \right. \tag{3.15b}$$

$$\left. - \frac{\rho}{2r_1 r_2}\left(\frac{1}{r_2}\frac{\partial}{\partial r_1} - \frac{1}{r_1}\frac{\partial}{\partial r_2} \right) \right] F_1' = 0$$

In order to show the Born-Oppenheimer limit of these equations we introduce the following transformation:

$$F_1' = H_1' e^{i\alpha/2} + i H_{-1}' e^{-i\alpha/2} \tag{3.16}$$

$$\tilde{F}_1' = -i H_1' e^{i\alpha/2} - H_{-1}' e^{-i\alpha/2} \tag{3.17}$$

where

$$\tan \alpha = \frac{(r_2^2 - r_1^2)\rho}{(r_2^2 - r_1^2)^2 - r_{12}^2(r_1^2 + r_2^2)} \tag{3.18}$$

This transformation has obviously not been pulled out of a hat. Rather it corresponds to a transformation of the Euler angles which will be further discussed in the Appendix A.

We now make this transformation in (3.15). Multiplying the transformed of (3.15b) by i and adding to the transformed of (3.15a) gives

$$\left[L'_{r_{12}} - \frac{2 r_{12}^2}{\rho^2} + \frac{2m_e}{\hbar^2} (E - V) \right] H_1^1 - \frac{2 r_{12}^2}{\rho^2} H_{-1}^1 = 0 \tag{3.19a}$$

Subtracting gives

$$\left[L'_{r_{12}} - \frac{2 r_{12}^2}{\rho^2} + \frac{2m_e}{\hbar^2} (E - V) \right] H_{-1}^1 - \frac{2 r_{12}^2}{\rho^2} H_1^1 = 0 \tag{3.19b}$$

Subtracting Eqs. (3.19a) and (3.19b), we get

$$\left[L'_{r_{12}} + \frac{2m_e}{\hbar^2} (E - V) \right] (H_1^1 - H_{-1}^1) = 0 \tag{3.20}$$

which according to (3.8b) corresponds to Σ states in the Born-Oppenheimer limit.

Adding Eqs. (3.19a) and (3.19b) we get

$$\left[L'_{r_{12}} - \frac{4 r_{12}^2}{\rho^2} + \frac{2m_e}{\hbar^2} (E - V) \right] (H_1^1 + H_{-1}^1) = 0 \tag{3.21}$$

which according to Eq. (3.8b) corresponds to Π states in the Born-Oppenheimer limit.

Therefore for $\ell = 1$ we get two Π states and one Σ state.

D. $\ell = 2$, even parity

Eq (2.21) in this case involves the radial functions F_2^0, F_2^2, and $\tilde{F}_2^2$. Making the transformation

$$F_2^0 = \frac{1+i}{\sqrt{2}} H_0^2 \tag{3.22}$$

$$F_2^2 = i\, H_2^2\, e^{i\alpha} + H_{-2}^2\, e^{-i\alpha} \tag{3.23}$$

$$\tilde{F}_2^2 = H_2^2\, e^{i\alpha} + iH_{-2}^2\, e^{-i\alpha} \tag{3.24}$$

yields three real equations for the functions H_2^2, H_{-2}^2, H_0^2. One can readily construct linear combinations of these equations which are the Σ, Π, and Δ states of H_2^+.

E. $\ell = 2$, odd parity

Here one makes the transformation

$$F_2^1 = -iH_1^2 e^{i\alpha/2} + H_{-1}^2\, e^{-i\alpha/2} \tag{3.25}$$

$$\tilde{F}_2^1 = -H_1^2\, e^{i\alpha/2} + iH_{-1}^2\, e^{-i\alpha/2} \tag{3.26}$$

The resultant equations can then be shown in a similar manner to be equivalent to Π and Δ states of H_2^+.

Therefore, it can be shown that for $\ell = 2$, there are Σ, Π, Δ even parity states and for odd parity there are Π and Δ states.

This checks the well-known rule that for an arbitrary ℓ all Λ states except $\Lambda = 0$ are doubly degenerate (positive-negative)[6], and for Σ states the parity of the ℓ equation which yields this state is given by

$$(-1)^{\ell + \kappa} = 1. \tag{3.27}$$

If one considers the finite mass of the nuclei, then the degeneracy of the $\Lambda \neq 0$ states is lifted giving rise to the Λ - doubling phenomenon[6]. Our results also conform the rule[6] $\Lambda \leq \ell$.

In order to facilitate the discussion of the p-μ-p molecule we also give the relation of the electronic gerade and ungerade classes to the three-body symmetries. This relation is

$$iE = \mathcal{P}\,\mathcal{E}_{12} \tag{3.28}$$

which can readily be verified two ways. First both the left and right sides have precisely the same effect on the Hamiltonian, and second if one starts with a spatial configuration of the nuclei and the electron, then the operation of iE will yield the same final configuration as $\mathcal{P}\mathcal{E}_{12}$.[7]

A specific example of the above is provided by $\ell = 0$ (there is only even parity in this case) and the $\ell = 1$, odd parity cases. We have shown above the radial equations in both cases approach the Σ

equations of H_2^+. Nevertheless the vector spherical harmonic portions of the complete wave functions are appropriate to $\ell = 0$ and $\ell = 1$ respectively, and are hence different. The lowest $\ell = 0$ wave function corresponds to the ground Σ_g state of H_2^+, whereas the lowest $\ell = 1$ odd parity wave function corresponds to the first excited rotational level of the Σ_g electronic state of H_2^+. It is the latter state which in the μ mesonic counterpart of H_2^+, namely the molecule $p - \mu - p$, is primarily responsible[8] for the absorption of μ mesons in hydrogen. The original calculation[9] which only corrects the Born-Oppenheimer approximation to the extent that the error is reduced from the order →

$(m_\mu/M_p)^{1/4}$ to the order (m_μ/M_p) gives a decay rate of about 560 sec^{-1} whereas the most recent experimental number[2] is $464 \pm 42\ sec^{-1}$. That the bulk of the discrepancy is in fact due to the Born-Oppenheimer approximation has been shown by a recent calculation of Wessel and Phillipson[3] who attacked the problem as a three-body problem and obtained a value of 480 sec^{-1}. Their variational calculation did in fact omit certain coupling terms in the radial equation but these omissions are of the order of $(m_\mu/M_p)^2$. (It should be noted that an accurate variational calculation has been made for this state in which all terms in the radial equations have been included[10]. The calculation was not primarily intended for this application.) Furthermore, we see that the ground state, Σ_g, is gerade ($iE = +1$) and is derived from the $\ell = 0$ equation which is necessarily even parity ($\varkappa = 0$). From (3.28) it follows that $\varepsilon_{12} = +1$, so that the three-body spatial function is symmetric and its spin antisymmetric (singlet), i.e., a para state. On the other hand the capture takes place from an $\ell = 1$ odd parity-state, the first rotational excited state of the Σ_g electronic state which according to (3.28) is $\varepsilon_{12} = -1$, i.e., a triplet or ortho state. Since the eigenvalue of $\mathcal{P}$ is $(-1)^\varkappa$ we can also write

$$iE = (-1)^\varkappa \varepsilon_{12} \qquad (3.29)$$

APPENDIX A

This appendix is concerned with the relation between the present Euler angles and another set of symmetric Euler angles that have been introduced[11,12]. This particular alternate set differs only as concerns ψ . Specifically it is measured from the line of nodes to the larger of the moments of inertia in the particle plane. Letting ψ_D be the alternative azimuth, our objective is to find ψ_D as a function ψ . We shall find that ψ_D depends additionally on r_1, r_2 and θ_{12}, the significance of which we shall discuss further at the end of this appendix.

The alternative definition of the azimuth is given in terms of a ratio of products of inertia in a coordinate system measured with respect to the center of mass. Letting $\underset{\sim}{\xi}_i$ be these coordinates of the three particles , we find

$$\underset{\sim}{\xi}_j = \underset{\sim}{r}_j + \underset{\sim}{\xi}_3 \qquad , \qquad j = 1, 2 \tag{A.1}$$

$$\underset{\sim}{\xi}_3 = - \frac{1}{\mu}(\mu_1 \underset{\sim}{r}_1 + \mu_2 \underset{\sim}{r}_2) \tag{A.2}$$

where μ_i , i = 1, 2, 3, are the masses of the three particles and

$$\mu = \sum_{i=1}^{3} \mu_i . \tag{A.3}$$

ξ_j $(j = 1, 2)$ are the vectors from the third particle to each of the identical particles (although this analysis allows all three masses to be different.) The components of the $\underset{\sim}{\xi_i}$ are defined by

$$\underset{\sim}{\xi_i} = \hat{i}' \xi_{ix} + \hat{j}' \xi_{iy} \tag{A.4}$$

where $\hat{i}'$ and $\hat{j}'$ are unit vectors along x'- and y'- axes in the particle plane. We have previously given, Eqs. (I15) and (I16), $\hat{r}_1$ and $\hat{r}_2$ in the $\hat{i}'$, $\hat{j}'$ coordinate system. Substitution of these relations into (A.1) and (A.2) gives the following relations for $\underset{\sim}{\xi_i}$:

$$\xi_{1x} = \left(1 - \frac{\mu_1}{\mu}\right) r_1 \sin\left(\Psi - \tfrac{1}{2}\theta_{12}\right) - \frac{\mu_2}{\mu} r_2 \sin\left(\Psi + \tfrac{1}{2}\theta_{12}\right) \tag{A.5}$$

$$\xi_{1y} = -\left(1 - \frac{\mu_1}{\mu}\right) r_1 \cos\left(\Psi - \tfrac{1}{2}\theta_{12}\right) + \frac{\mu_2}{\mu} r_2 \cos\left(\Psi + \tfrac{1}{2}\theta_{12}\right) \tag{A.6}$$

$$\xi_{2x} = -\frac{\mu_1}{\mu} r_1 \sin\left(\Psi - \tfrac{1}{2}\theta_{12}\right) + \left(1 - \frac{\mu_2}{\mu}\right) r_2 \sin\left(\Psi + \tfrac{1}{2}\theta_{12}\right) \tag{A.7}$$

$$\xi_{2y} = \frac{\mu_1}{\mu} r_1 \cos\left(\Psi - \tfrac{1}{2}\theta_{12}\right) - \left(1 - \frac{\mu_2}{\mu}\right) r_2 \cos\left(\Psi + \tfrac{1}{2}\theta_{12}\right) \tag{A.8}$$

$$\xi_{3x} = -\frac{\mu_1}{\mu} r_1 \sin(\Psi - \tfrac{1}{2}\theta_{12}) - \frac{\mu_2}{\mu} r_2 \sin(\Psi + \tfrac{1}{2}\theta_{12}) \tag{A.9}$$

$$\xi_{3y} = \frac{\mu_1}{\mu} r_1 \cos(\Psi - \tfrac{1}{2}\theta_{12}) + \frac{\mu_2}{\mu} r_2 \cos(\Psi + \tfrac{1}{2}\theta_{12}) \tag{A.10}$$

The definition of Ψ_D is given by[13]

$$\tan 2\Psi_D = \frac{-2 D_{xy}}{D_{xx} - D_{yy}} \tag{A.11}$$

where

$$D_{xy} = \sum_{i=1}^{3} \mu_i \xi_{ix} \xi_{iy} \tag{A.12}$$

$$D_{xx} = \sum_{i=1}^{3} \mu_i \xi_{iy}^2 \tag{A.13}$$

$$D_{yy} = \sum_{i=1}^{3} \mu_i \xi_{ix}^2 \tag{A.14}$$

Substituting (A.5) - (A.10) into (A.12) - (A.14) yields

$$\tan 2\Psi_D = \Big[\mu_1 (1 - \frac{\mu_1}{\mu})\, r_1^2 \sin(2\Psi - \theta_{12}) + \mu_2 (1 - \frac{\mu_2}{\mu})\, r_2^2 \sin(2\Psi + \theta_{12})$$

$$- \frac{2\mu_1\mu_2}{\mu}\, r_1 r_2 \sin 2\Psi \Big] \Big[\mu_1 (1 - \frac{\mu_1}{\mu})\, r_1^2 \cos(2\Psi - \theta_{12}) \qquad \text{(A.15)}$$

$$+ \mu_2 (1 - \frac{\mu_2}{\mu})\, r_2^2 \cos(2\Psi + \theta_{12}) - \frac{2\mu_1\mu_2}{\mu}\, r_1 r_2 \cos 2\Psi \Big]^{-1}$$

Specializing to H_2^+ limit, we have

$$\mu_1 = \mu_2 = M_p \to \infty$$

$$\mu_3 = m_e$$

$$\tan 2\Psi_D = \frac{[(r_1^2 + r_2^2)\cos\theta_{12} - 2 r_1 r_2] \sin 2\Psi + (r_2^2 - r_1^2)\sin\theta_{12} \cos 2\Psi}{(r_1^2 - r_2^2)\sin\theta_{12} \sin 2\Psi + [(r_1^2 + r_2^2)\cos\theta_{12} - 2 r_1 r_2] \cos 2\Psi}$$

$$= \tan(2\Psi + \alpha), \qquad \text{(A.16)}$$

where

$$\tan\alpha = \frac{(r_2^2 - r_1^2)\sin\theta_{12}}{(r_1^2+r_2^2)\cos\theta_{12} - 2r_1r_2} . \tag{A.17}$$

Using

$$\cos\theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1r_2} , \tag{A.18}$$

we find

$$\tan\alpha = \frac{(r_2^2 - r_1^2)\rho}{(r_1^2 - r_2^2)^2 - r_{12}^2(r_1^2+r_2^2)} \tag{A.19}$$

With the relation (A.16) one can then transform the wave function[12]

$$\underset{\sim}{\Psi} = \sum_{k=-\ell}^{\ell} H_k^{\ell}(r_1, r_2, r_{12}) \, \mathcal{D}_{\ell}^{m,k}(\theta, \Phi, \Psi) \tag{A.20}$$

into our form Eq. (2.14), from which one derives the relation between

$f_\ell^{\kappa\pm}$ (and hence F_ℓ^{κ}) and H_k^{ℓ} .

The radial equations which result are consequently precisely those that one would get directly from the formulae of Diehl et. al.[9] in the H_2^+ limit. The simplicity of their equations from the point of view of this limit stems from the fact that the axis to which $\mathfrak{F}_D$ is measured becomes identical with the line joining the nuclei, i.e., the z-axis, in the Born-Oppenheimer approximation.

In the case of all finite masses, however, there arises an additional group of terms in their equations. A comparison with our equations indicates that in general their equations are more complicated than ours. In particular some of the coefficients have a more complicated analytic behavior. We believe this is related to an argument in I which stated that because our Euler angles depend only on the unit vectors $\hat{r}_1$ and $\hat{r}_2$ and not on the magnitudes of r_1 and r_2, we think our Euler angles are superior; for they retain the separation between angular and radial parts which was implicit in the expansion of the complete wave function itself (cf. (2.14) and (A.20)). The suggestion that we are making here is that a concrete manifestation of such a superiority may reside precisely in the differences in the analytic structure of the respective radial equations.

The dependence of $\mathfrak{F}_D$ on r_1 and r_2 is explicitly exhibited in Eqs. (A.16) and (A.17). In Appendix III of reference 1 we derived the relation between ours and the Hylleraas-Breit Euler angles[14,15].

The latter have the disadvantage of not being symmetrical, but they too depend only on the unit vectors $\hat{r}_1$ and $\hat{r}_2$. Therefore the relations between the respective Euler angles are independent of r_1 and r_2. According to the above argument we do not expect any significant difference in the analytic properties of Breit's (P state) radial equations[15] as compared to our own.

Appendix B

For three unequal mass particles, the kinetic energy in the center of mass system is

$$T = -\frac{1}{2\mu_1}\nabla^2_{r_1} - \frac{1}{2\mu_2}\nabla^2_{r_2} - \frac{1}{M}\underset{\sim}{\nabla}_{r_1}\cdot\underset{\sim}{\nabla}_{r_2} \tag{B.1}$$

where

$$\mu_1 = \frac{m_1 M}{m_1 + M} \tag{B.2}$$

$$\mu_2 = \frac{m_2 M}{m_2 + M} \tag{B.3}$$

The Schrödinger equation in the c.m. system is thus

$$\left[\nabla^2_{r_1} + \mu_1/\mu_2\,\nabla^2_{r_2} + \frac{2\mu_1}{M}\underset{\sim}{\nabla}_{r_1}\cdot\underset{\sim}{\nabla}_{r_2} + \frac{2\mu_1}{\hbar^2}(E-V)\right]\Psi = 0\,. \tag{B.4}$$

It has been shown how the individual Laplacian may be written in terms of the Euler angles and residual coordinates r_1 , r_2 , θ_{12} :

$$\nabla^2_{r_1} = \frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1 + \frac{1}{r_1^2}\left\{\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}} + F_1(\theta,\Phi,\psi)\right\} \tag{B.5}$$

$$\nabla^2_{r_2} = 1/r_2 \frac{\partial^2}{\partial r_2^2} r_2 + \frac{1}{r_2^2}\left\{ 1/\sin\theta_{12} \frac{\partial}{\partial\theta_{12}} \sin\theta_{12} \frac{\partial}{\partial\theta_{12}} + F_2(\theta, \Phi, \psi)\right\} \qquad (B.6)$$

where F_1 and F_2 are given in Eqs. (I59, I62). Knowing then the effect of F_1, F_2 and the cross term $\underset{\sim}{\nabla_{r_1}} \cdot \underset{\sim}{\nabla_{r_2}}$ on the vector spherical harmonics via their representation in terms of the Λ_1 , Λ_2 operators in (I63, 64) and (2.13), one may readily derive the radial equations for the general case. As coupled equations in terms of the residual coordinates r_1, r_2, θ_{12}, the radial equations are obtained by making the following substitution in (2.15):

$$\mu \rightarrow \mu_1 \qquad (B.7)$$

$$r_1^{-2} \pm r_2^{-2} \rightarrow r_1^{-2} \pm \mu_1/\mu_2 \; r_2^{-2} \qquad (B.8)$$

$$L_{\theta_{12}} \rightarrow \bar{L}_{\theta_{12}} = \frac{1}{r_1}\frac{\partial^2}{\partial r_1^2} r_1 + \mu_1/\mu_2 \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2} r_2$$

$$+ \left(\frac{1}{r_1^2} + \frac{\mu_1}{\mu_2}\frac{1}{r_2^2}\right)\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}} \qquad (B.9)$$

Since for $m_1 \neq m_2$ the equations are no longer symmetric with respect to $r_1 \rightleftarrows r_2$, it is necessary to solve the equations for all values of r_1

and r_2 (as opposed to, say, $r_1 \geqslant r_2$ and an appropriate boundary condition when m_1 is identical to m_2). By virtue of this there is no advantage in defining functions $F_\ell^{\varkappa}$ and $\tilde{F}_\ell^{\varkappa}$ as they will also be described by a coupled set of equations, rather than a single equation (2.21) for the identical particle case. For this reason we give below the equations in terms of the coupled $f_\ell^{\varkappa\pm}$ functions, but involving the coordinates r_1, r_2, r_{12}.

$$
\Big[L_{r_{12}} + \frac{2\mu_1}{\hbar^2}(E-V) \Big] f_\ell^{\varkappa+} - \Big(\frac{1}{r_1^2} + \frac{\mu_1}{\mu_2}\frac{1}{r_2^2}\Big) \Big[\Big\{ \big(\ell(\ell+1) - \varkappa^2\big) \frac{2 r_1^2 r_2^2}{\rho^2}
$$

$$
+ \frac{\varkappa^2}{4} - \frac{r_1 r_2}{2\rho^2}(r_1^2 + r_2^2 - r_{12}^2)\, \delta_{1\varkappa}\, \ell(\ell+1) \Big\} f_\ell^{\varkappa+}
$$

$$
+ \frac{r_1 r_2}{2\rho^2}(r_1^2 + r_2^2 - r_{12}^2) \Big\{ B_\ell^{\varkappa+2} f_\ell^{(\varkappa+2)+} + (1 - \delta_{0\varkappa} - \delta_{1\varkappa} + \delta_{2\varkappa})\, B_{\ell\varkappa} f_\ell^{(\varkappa-2)+} \Big\} \Big]
$$

$$
+ \Big(\frac{1}{r_1^2} - \frac{\mu_1}{\mu_2}\frac{1}{r_2^2}\Big) \Big[- \Big\{ \frac{\varkappa}{2} \Big(\frac{r_1^2 + r_2^2 - r_{12}^2}{\rho} + \frac{\rho}{r_{12}} \frac{\partial}{\partial r_{12}} \Big)
$$

$$
+ \ell(\ell+1)\, \delta_{1\varkappa} \frac{r_1 r_2}{2\rho} \Big\} f_\ell^{\varkappa-} + \frac{r_1 r_2}{2\rho} \Big\{ B_\ell^{\varkappa+2} f_\ell^{(\varkappa+2)-}
$$

$$
- (1 - \delta_{0\varkappa} - \delta_{1\varkappa} - \delta_{2\varkappa})\, B_{\ell\varkappa} f_\ell^{(\varkappa-2)-} \Big\} \Big]
$$

$$
+ \frac{2\mu_1}{m_3} \Big[\Big\{ (r_1^2 + r_2^2 - r_{12}^2) \Big(\frac{\ell(\ell+1) - \varkappa^2}{\rho^2} - \frac{\varkappa^2}{8 r_1^2 r_2^2} \Big) - \ell(\ell+1)\, \delta_{1\varkappa} \frac{r_1 r_2}{\rho^2} \Big\} f_\ell^{\varkappa+}
$$

$$
+ \frac{r_1 r_2}{\rho^2} \Big\{ B_\ell^{\varkappa+2} f_\ell^{(\varkappa+2)+} + (1 - \delta_{0\varkappa} - \delta_{1\varkappa} + \delta_{2\varkappa}) f_\ell^{(\varkappa-2)+} \Big\}
$$

$$+ \frac{x\rho}{4r_1r_2}\left(\frac{1}{r_1}\frac{\partial}{\partial r_2} - \frac{1}{r_2}\frac{\partial}{\partial r_1} + \frac{r_2^2 - r_1^2}{r_1r_2}\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} \right) f_\ell^{x-} \Big] = 0 \tag{B.10}$$

$$\Big[\bar{L}'_{r_{12}} + \frac{2\mu_1}{\hbar^2}(E - V) \Big] f_\ell^{x-} - \left(\frac{1}{r_1^2} + \frac{\mu_1}{\mu_2}\frac{1}{r_2^2} \right) \Big[\Big\{ (\ell(\ell+1) - x^2)\, 2\frac{r_1^2r_2^2}{\rho^2}$$

$$+ \frac{x^2}{4} + \frac{r_1r_2}{2\rho^2}(r_1^2 + r_2^2 - r_{12}^2)\,\delta_{1x}\,\ell(\ell+1) \Big\} f_\ell^{x-}$$

$$+ \frac{r_1r_2}{2\rho^2}(r_1^2 + r_2^2 - r_{12}^2)\Big\{ (1-\delta_{0x})\, B_\ell^{x+2} f_\ell^{(x+2)-} + (1 - \delta_{0x} - \delta_{1x} - \delta_{2x})\, B_{\ell x} f_\ell^{(x-2)-} \Big\}\Big]$$

$$+ \left(\frac{1}{r_1^2} - \frac{\mu_1}{\mu_2}\frac{1}{r_2^2} \right) \Big[\Big\{ \frac{x}{2}\left(\frac{r_1^2 + r_2^2 - r_{12}^2}{\rho} + \frac{\rho}{r_{12}}\frac{\partial}{\partial r_{12}} \right) - \ell(\ell+1)\,\delta_{1x}\frac{r_1r_2}{2\rho} \Big\} f_\ell^{x+}$$

$$- \frac{r_1r_2}{2\rho}\Big\{ (1-\delta_{0x})\, B_\ell^{x+2} f_\ell^{(x+2)+} - (1 - \delta_{0x} - \delta_{1x} + \delta_{2x})\, B_{\ell x} f_\ell^{(x-2)+} \Big\}\Big]$$

$$+ \frac{2\mu_1}{m_3}\Big[\Big\{ (r_1^2 + r_2^2 - r_{12}^2)\left(\frac{\ell(\ell+1) - x^2}{\rho^2} - \frac{x^2}{8r_1^2r_2^2} \right) + \ell(\ell+1)\,\delta_{1x}\frac{r_1r_2}{\rho^2} \Big\} f_\ell^{x-}$$

$$+ \frac{r_1r_2}{\rho^2}\Big\{ (1-\delta_{0x})\, B_\ell^{x+2} f_\ell^{(x+2)-} + (1 - \delta_{0x} - \delta_{1x} - \delta_{2x}) B_{\ell x} f_\ell^{(x-2)-} \Big\}$$

$$+ \frac{x\rho}{4r_1r_2}\left(\frac{1}{r_2}\frac{\partial}{\partial r_1} - \frac{1}{r_1}\frac{\partial}{\partial r_2} + \frac{r_1^2 - r_2^2}{r_1r_2}\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}} \right) f_\ell^{x+} \Big] = 0 \tag{B.11}$$

where

$$\bar{L}'_{r_{12}} = \frac{1}{r_1}\frac{\partial^2}{\partial r_1^2} r_1 + \frac{\mu_1}{\mu_2}\frac{1}{r_2}\frac{\partial^2}{\partial r_2^2} r_2 + \frac{\mu_1}{\mu_{12}}\frac{1}{r_{12}}\frac{\partial^2}{\partial r_{12}^2} r_{12} + \frac{\mu_1}{m_1}\frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}}$$

$$+ \frac{\mu_1}{m_2}\frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}} + \frac{\mu_1}{m_3}\frac{r_1^2 + r_2^2 - r_{12}^2}{r_1 r_2}\frac{\partial^2}{\partial r_1 \partial r_2} \tag{B.12}$$

and

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \tag{B.13}$$

The resulting radial equations are invariant (except for a relative phase factor which does not affect the eigenvalue spectrum) under the simultaneous exchange of $k_1 \rightleftarrows k_2$ and $m_1 \rightleftarrows m_2$. However the equations are not (formally) invariant under a simultaneous permutation of all three particles (i.e., simultaneous cyclic permutations of m_1, m_2, m_3 and r_1, r_2, r_{12}). This is apparently due to the fact that our choice of Euler angles singles out one particle, the particle with mass M, as the instantaneous origin. This in turn means that the line to which the azimuth Φ is measured depends asymmetrically on which particle we call the origin. As opposed to this the Euler angles of Holmberg[11] and Diehl et al.[12] are invariant under the operation, and their radial equations are also.

Since, however, the transformation between the respective radial functions can be worked out from Eq. (A.15), this additional symmetry can readily be recovered. It would seem that a more practical criterion of the utility of the equations is the analytic properties of the equations themselves. In this respect the discussion near the end of Appendix A may be more relevant.

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TABLE I

Coefficients of the Angular Derivatives in the Cross Term of the Kinetic Energy.[a]

Coefficient	Derivative	Coefficient	Derivative
$-\cos\,\theta_{12}$	$\frac{\partial^2}{\partial\theta_{12}{}^2}$	$\frac{-\cot\,\theta\,\sin\,2\,\Psi}{\sin^2\,\theta_{12}}$	$\frac{\partial^2}{\partial\theta\partial\Psi}$
$\frac{\cos\,2\,\Psi\,-\,\cos\,\theta_{12}}{2\,\sin^2\theta_{12}}$	$\frac{\partial^2}{\partial\theta^2}$	$\frac{\cos\,\theta\,(\cos\,\theta_{12}\,+\,\cos\,2\,\Psi)}{\sin^2\,\theta\,\sin^2\theta_{12}}$	$\frac{\partial^2}{\partial\Psi\partial\Phi}$
$-\,\sin\,\theta_{12}$	$\frac{\partial^2}{\partial r_{\binom{1}{2}}\partial\theta_{12}}$	$\frac{\cos\,\theta_{12}}{4}\,-\,\frac{\cot^2\theta}{2\,\sin^2\theta_{12}}(\cos\theta_{12}+\cos2\Psi)$	$\frac{\partial^2}{\partial\Psi^2}$
$-\,\frac{1}{2}\,\sin\,\theta_{12}$	$\frac{\partial^2}{\partial r_1\partial\Psi}$	$-\,\frac{1}{\sin\,\theta_{12}}$	$\frac{\partial}{\partial\theta_{12}}$
$+\,\frac{1}{2}\,\sin\,\theta_{12}$	$\frac{\partial^2}{\partial r_2\partial\Psi}$	$\frac{-\,\cot\,\theta}{2\,\sin^2\theta_{12}}(\cos\,2\,\Psi\,+\,\cos\,\theta_{12})$	$\frac{\partial}{\partial\theta}$
$\frac{\sin\,2\,\Psi}{\sin^2\,\theta_{12}\,\sin\,\theta}$	$\frac{\partial^2}{\partial\theta\partial\Phi}$	$\frac{-\,\cot\,\theta\,\sin\,2\,\Psi}{\sin\,\theta\,\sin^2\,\theta_{12}}$	$\frac{\partial}{\partial\Phi}$
$-\,\frac{(\cos\,\theta_{12}+\cos\,2\Psi)}{2\sin^2\theta_{12}\,\sin^2\theta}$	$\frac{\partial^2}{\partial\Phi^2}$	$\frac{\sin\,2\,\Psi}{2\,\sin^2\theta_{12}}(1\,+\,2\,\cot^2\,\theta)$	$\frac{\partial}{\partial\Psi}$

[a]The dependence on r_1 and r_2 is not included. All unincluded partial derivatives have zero coefficients.