The triatomic hydrogen ion H_3^+. By H. S. W. MASSEY, Trinity College. (Communicated by Mr N. F. MOTT.)

[*Read* 18 May 1931.]

The advent of quantum mechanics has provided a means of treating the interaction of atoms and the formation* of molecules and has had very many successes in this field. In particular the phenomenon of the saturation of valence forces appears as a natural consequence of the theory. Nevertheless there are very many difficulties still to be overcome.

In the first calculations of Heitler and London†, which applied to the interaction of normal atoms in S states, it was found that the characteristic of the atom of greatest importance in determining the nature of the interaction was the electronic symmetry of the states considered. On this, London‡ based the rule that the number of free valences of an atom is given by the number of its unpaired electrons, the pairing of electrons corresponding to cancelling of spin angular momenta and representing the saturation of a valence bond. This theory certainly seems correct for atoms in S states, but for atoms not in such states it is found to have no general application. Thus for the interaction of excited atoms, Kemble and Zener§ found that the nuclear symmetry characteristic was the deciding factor, while for the case of atoms in P states‖ it appears that orbital angular momentum considerations are of considerable importance.

The extension of the theory to polyatomic molecules has been commenced by Heitler and Rumer¶, but the importance of nuclear symmetry has not been considered. No case of systems with more than two nuclei has been considered so far; and it thus is of interest to consider the simplest possible case of a triatomic molecule, the ion H_3^+. This ion is known to exist in discharge tubes and its mass has been measured by Aston in his mass spectrograph**. We shall show here that nuclear symmetry considerations are the most important, and decide the stability of the molecule.

1. *Perturbation method.* The method of perturbation adopted is a simple generalisation of that used for diatomic molecules. We

* *Vide* Heitler, *Phys. Zeit.* 31, p. 185 (1930).
† *Zeit. für Phys.* 44, p. 455 (1927).
‡ *Ibid.* 46, p. 455 (1928).
§ *Phys. Rev.* 33, p. 512 (1929).
‖ Heitler, *Naturwiss.* 17, p. 546 (1929); Bartlett, *Phys. Rev.* 37, p. 507 (1931).
¶ *Gött. Nach.* p. 277 (1930); *Zeit. für Phys.* 68, p. 12 (1931).
** Aston, *Isotopes.*

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start with two separated systems, taking the product of their wave functions to represent the state of the system as a whole. On bringing them into interaction we must take now as zero order approximation a linear combination of these products, each corresponding to identical states of the total system but with equivalent particles interchanged. The matrix element of the interaction energy with respect to this wave function gives the corresponding perturbation energy. The appropriate linear combination is obtained by solving a secular equation which may be treated by the methods of group theory.

In the case of the triatomic hydrogen ion we have the choice of two possibilities for our unperturbed system. We may take either a hydrogen molecular ion, H_2^+, and a hydrogen atom, H, in interaction, or a hydrogen molecule, H_2, and a proton, H^+. Actually we should take a linear combination of the wave functions for the two cases but, if we work them out separately, we may determine which, if either, is important in deciding the stability of the system. If both give interaction energies with low minima under the same geometrical conditions, we may suppose the true state of affairs to be a combination of both. If only one gives binding, it is the important one. We thus consider the two cases separately, but may proceed in the same manner with both methods up to a certain point.

We denote the distances of the electron from the nuclei 1, 2, 3 by r, p, q respectively; the distances of the corresponding nuclei from each other by R_{12}, R_{13}, R_{23} and the electron distances by r_{12}, r_{13}, r_{23}. The wave function of the separated system is denoted by $\psi(123)$, the numbers referring to the nuclei. Other possible wave functions will be $\psi(321)$ and $\psi(231)$, since the nuclei are equivalent. As initial wave functions we have then

$$a\psi(123) + b\psi(321) + c\psi(231).$$

Now in the case of three equivalent particles we can have wave functions with the Hund symmetry characters $\Psi(\overline{123})$, symmetrical in all these particles, or $\Psi(\overline{12}3)$ symmetrical in two only, for a wave function antisymmetrical in all three can only be identically zero. In the case of particles obeying the Fermi-Dirac statistics the first of these is excluded, for it would require the wave function of certain other coordinates describing the motion to be antisymmetric in all three, a possibility which could only be satisfied by the function vanishing. Thus for the hydrogen nuclei, which are well known to have spin and so obey the Fermi-Dirac statistics, we can only have the function $\Psi(\overline{12}3)$. This is exactly similar to the case of the lithium atom, where we have an electronic wave function for the lowest doublet state with just the same symmetry

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character, or to the case of interaction of hydrogen and helium atoms. Then just as for these cases we must take one or other of the functions

$$\Psi = \frac{1}{\sqrt{3}}\{\psi(123) + \epsilon\psi(312) + \epsilon^2\psi(231)\},$$

or

$$\frac{1}{\sqrt{3}}\{\psi(123) + \epsilon^2\psi(312) + \epsilon\psi(231)\},$$

where $\epsilon^3 = 1$, giving rise to the same energies.

The Schrödinger equation of the system is

$$\left\{\nabla_1^2 + \nabla_2^2 + \frac{8\pi^2 m}{h^2}(E - V)\right\}\Psi = 0,$$

where

$$V = \frac{e^2}{R_{12}} + \frac{e^2}{R_{13}} + \frac{e^2}{R_{23}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_1} - \frac{e^2}{p_1} - \frac{e^2}{q_1} - \frac{e^2}{r_2} - \frac{e^2}{p_2} - \frac{e^2}{q_2}.$$

The energy of the system corresponding to the function ψ is then given by

$$E = \frac{\int V\Psi\bar{\Psi}dv}{\int\Psi\bar{\Psi}dv}. \qquad \text{.....(1)}$$

Let us now consider the two possible initial systems:

(*a*) H_2^+ and H. We have here, if electron 1 is attached to nuclei 1 and 2, and electron 2 to nucleus 3,

$$\psi(123) = \phi_1(12)\chi_2(3) \pm \phi_2(12)\chi_1(3),$$

where $\phi_1(12)$ is a solution of the equation

$$\nabla_1^2\phi_1 + \frac{8\pi^2 m}{h^2}\left(E_0 - \frac{e^2}{R_{12}} + \frac{e^2}{r_1} + \frac{e^2}{p_1}\right)\phi_1 = 0,$$

so that the energy of H_2^+, at separation d, is

$$E_0 = \int\left(\frac{e^2}{R_{12}} - \frac{e^2}{r_2} - \frac{e^2}{p_2}\right)\phi_1(12)\,\bar{\phi}_1(12)\,dv_2 \Big/ \int|\phi_1(12)|^2\,dv,$$

and $\chi_2(3)$ is a solution of the equation

$$\nabla_2^2\chi_2 + \frac{8\pi^2 m}{h^2}\left(E_1 + \frac{e^2}{q}\right)\chi_2 = 0,$$

where E_1 is the energy of the ground state of hydrogen.

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Substituting in (1) we now have

$$E = \frac{\left\{\frac{e^2}{3}\iint\left(\frac{1}{R_{12}}-\frac{1}{r_1}-\frac{1}{p_1}-\frac{1}{q_1}+\frac{1}{R_{23}}+\frac{1}{r_{12}}-\frac{1}{r_2}-\frac{1}{p_2}-\frac{1}{q_2}+\frac{1}{R_{31}}\right)\right.}{\iint|\psi(123)+\epsilon\psi(321)+\epsilon^2\psi(213)|^2\,dv_1\,dv_2} \left.\times|\psi(123)+\epsilon\psi(321)+\epsilon^2\psi(213)|^2\,dv_1\,dv_2\right\}$$

$$= E_0 + E_1 + \frac{e^2}{R_{13}} + \frac{e^2}{R_{23}}$$

$$+ \frac{e^2\iint\left(\frac{1}{r_{12}}-\frac{1}{q_1}-\frac{1}{r_2}-\frac{1}{p_2}\right)\{\psi(123)^2-\psi(123)\,\psi(321)\}\,dv_1\,dv_2}{\iint\{\psi(123)^2-\psi(123)\,\psi(321)\}\,dv_1\,dv_2}, \quad \ldots\ldots(2)$$

the nuclear separations being taken to be equal in this symmetrical treatment.

It is of interest to note that if the symmetrical wave function

$$\Psi = \frac{1}{\sqrt{3}}\{(\psi(123)+\psi(321)+\psi(213)\}$$

had been allowable we should have had

$$E = E_0 + E_1 + \frac{e^2}{R_{13}} + \frac{e^2}{R_{23}}$$

$$+ \frac{e^2\iint\left(\frac{1}{r_{12}}-\frac{1}{q_1}-\frac{1}{r_2}-\frac{1}{p_2}\right)\{\psi(123)^2+2\psi(123)\,\psi(321)\}\,dv_1\,dv_2}{\iint\{\psi(123)^2+2\psi(123)\,\psi(321)\}\,dv_1\,dv_2}, \quad \ldots\ldots(3)$$

a different form from (2), for here the exchange term

$$\iint\left(\frac{1}{r_{12}}-\frac{1}{q_1}-\frac{1}{r_2}-\frac{1}{p_2}\right)\psi(123)\,\psi(321)\,dv_1 dv_2$$

is added to the Coulomb term, whereas above it is subtracted.

(*b*) H_2 and H^+. Proceeding in exactly the same way with an initial system consisting of a proton and hydrogen molecule we have again

$$E = E_2 - I + J + \frac{e^2}{R_{13}} + \frac{e^2}{R_{23}},$$

where E_2 is the energy of the hydrogen molecule and

$$\left.\begin{aligned} I &= e^2\int\left(\frac{1}{q_1}+\frac{1}{q_2}\right)\psi_{H_2}{}^2(12)\,dv \\ &\quad \div\int\{\psi_{H_2}{}^2(12)-\psi_{H_2}(12)\,\psi_{H_2}(23)\}\,dv_1\,dv_2 \\ J &= e^2\int\left(\frac{1}{q_1}+\frac{1}{q_2}\right)\psi_{H_2}(12)\,\psi_{H_2}(23)\,dv \\ &\quad \div\int\{\psi_{H_2}{}^2(12)-\psi_{H_2}(12)\,\psi_{H_2}(23)\}\,dv_1\,dv_2 \end{aligned}\right\} \ldots(4)$$

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where $\psi_{H_2}(12)$ is the wave function of a hydrogen molecule with nuclei 1 and 2.

It is clear from the form of the above expressions for E that it is much simpler to start with a hydrogen molecule and proton than with the ion and atom, since the integrals involved in the former case are much less complicated, there being less perturbation to take into account. In particular the Coulomb interaction between the two electrons does not appear. For this reason we shall confine the calculation to this case, but we may make the method more general by including the possibility of both electrons having the same spin. In the case of ion and atom we allowed for this by taking the wave function ψ to be symmetric or antisymmetric in the electrons. If we start with a molecule, we assume the spins to be antiparallel, the state with parallel spins giving rise to no stable state. We may include the other possibility by taking ψ_{H_2} to be either the wave function of the $1^1\Sigma$ or $1^3\Sigma$ state of the molecule, the latter state being in the continuous spectrum. If it should turn out that the state of H_3^+ formed from the latter is the stable one, then the ion can only be formed by collision of H_2^+ and H the electrons having parallel spins; if it is not stable, then either H_2 and H^+ or H_2^+ and H^+ with antiparallel spins may combine on collision to produce H_3^+. If neither of these gives a stable molecule we must regard H_3^+ as a polarisation compound.

2. *Calculation of Interaction Energy.* We have approximately

$$\psi_{H_2}(12) = e^{-\lambda(r_1+p_2)} \pm e^{-\lambda(r_2+p_1)}, \quad \lambda = \frac{1}{a_0}. \qquad \ldots\ldots(5)$$

Substituting in the expression (4) we have then

$$NI = I_1 \pm I_2,$$

where
$$I_1 = 2e^2 \iint \left(\frac{1}{q_1} + \frac{1}{q_2}\right) e^{-2\lambda(r_1+p_2)}\, dv_1\, dv_2, \qquad \ldots\ldots(6)$$

$$I_2 = 2e^2 \iint \left(\frac{1}{q_1} + \frac{1}{q_2}\right) e^{-\lambda(r_1+p_1+p_2+r_2)}\, dv_1\, dv_2; \qquad \ldots\ldots(7)$$

$$NJ = J_1 \pm J_2,$$

where
$$J_1 = 2e^2 \iint \left(\frac{1}{q_1} + \frac{1}{q_2}\right) e^{-\lambda(r_1+p_1+p_2+q_2)}\, dv_1\, dv_2, \qquad \ldots\ldots(8)$$

$$J_2 = 2e^2 \iint \left(\frac{1}{q_1} + \frac{1}{q_2}\right) e^{-\lambda(r_2+q_2+2p_1)}\, dv_1\, dv_2, \qquad \ldots\ldots(9)$$

N being given by

$$N = 2 \iint \{e^{-2\lambda(r_1+p_2)} \pm e^{-\lambda(r_1+p_1+p_2+r_2)} - e^{-\lambda(r_1+p_1+p_2+q_2)} \mp e^{-\lambda(r_2+q_2+2p_1)}\}\, dv_1\, dv_2.$$

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Since $$\int e^{-2\lambda(r_1+p_2)}\,dv_1\,dv_2 = \frac{\pi^2}{\lambda^6},$$

$$\int e^{-\lambda(r_1+p_1+p_2+q_1)}\,dv_1\,dv_2 = \frac{\pi^2}{\lambda^6}S^2,$$

where $$S = (1+\lambda d+\tfrac{1}{3}\lambda^2 d^2)\,e^{-2\lambda d},$$

d being the nuclear separation, assumed to be the same for all nuclei, we have

$$N = \frac{2\pi^2}{\lambda^6}(1-S) \qquad \text{electron spins parallel,}$$

$$(1-2S^2+S) \qquad \text{,,} \qquad \text{,,} \qquad \text{antiparallel.}$$

From (6),

$$I_1 = 4e^2\int\frac{1}{q_1}e^{-2\lambda r_1}\,dv_1\int e^{-2\lambda p_2}\,dv_2$$

$$= \frac{4\pi}{\lambda^3}e^2\int\frac{1}{q_1}e^{-2\lambda r_1}\,dv_1.$$

Expanding $\dfrac{1}{q_1}$ in harmonics with R_{12} as axis we have

$$\frac{1}{q_1} = \Sigma\,\gamma_n(r_1,d)\,P_n(\cos\theta_1)\,P_n(\cos\theta),$$

$$\gamma_n(r_1,d) = \frac{{r_1}^n}{d^{n+1}} \qquad r_1 < d$$

$$= \frac{d^n}{{r_1}^{n+1}} \qquad r_1 > d;$$

θ is the angle that the line joining nuclei 1 and 3 makes with that joining 1 and 2.

The orthogonality of the harmonics then reduces the integral to

$$\int\frac{1}{q_1}e^{-2\lambda r_1}\,dv_1 = 4\pi\int_0^\infty\gamma_0(r_1,d)\,e^{-2\lambda r_1}{r_1}^2\,dv_1$$

$$= \frac{\pi}{\lambda^3}\left[\frac{1-e^{-2\lambda d}}{d}-\lambda e^{-2\lambda d}\right];$$

$$I_1 = \frac{4\pi^2e^2}{\lambda^6}\left[\frac{1-e^{-2\lambda d}}{d}-\lambda e^{-2\lambda d}\right].$$

From (7),

$$I_2 = 4e^2\int\frac{1}{q_1}e^{-\lambda(r_1+p_1)}\,dv_1\int e^{-\lambda(r_2+p_2)}\,dv_2$$

$$= \frac{4\pi e^2}{\lambda^3}S\int\frac{1}{q_1}e^{-\lambda(r_1+p_1)}\,dv_1.$$

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Changing to elliptic coordinates $\rho_1 = \frac{r_1 + p_1}{d}$, $\mu_1 = \frac{r_1 - p_1}{d}$ with nuclei 1, 2 as foci, we have

$$I_2 = \frac{4\pi e^2 S}{\lambda^3} \frac{d^3}{8} \int \frac{1}{q_1} e^{-\lambda \rho_1 d} (\rho_1^2 - \mu_1^2)\, d\rho\, d\mu\, d\phi.$$

For $\frac{1}{q_1}$ we use Neumann's expansion*

$$\frac{1}{q_1} = \frac{2}{d} \sum_{\tau=0}^{\infty} \sum_{\nu=0}^{\tau} D_{\tau\nu} P_\tau^\nu(\rho)\, Q_\tau^\nu(\rho_1)\, P_\tau^\nu(\mu)\, P_\tau^\nu(\mu_1) \cos \nu(\phi_1 - \phi) \left\{ \begin{array}{l} \rho_1 > \rho \\ Q_\tau^\nu(\rho)\, P_\tau^\nu(\rho_1) \quad \rho_1 < \rho; \end{array} \right.$$

$$D_{\tau\nu} = (-1)^\nu \epsilon_\nu \frac{2\tau + 1}{2} \left\{ \frac{\Pi(\tau - \nu)}{\Pi(\tau + \nu)} \right\}^2, \quad \epsilon_0 = 1, \quad \epsilon_1 = \epsilon_2 = \epsilon_n = 2,$$

ρ, μ, ϕ being the elliptic coordinates of nucleus 3. This gives

$$I_2 = \frac{2\pi^2 e^2 S d^2}{\lambda^3} \left[\int_1^\rho e^{-\lambda d \rho_1} \{(\rho_1^2 - \tfrac{1}{3}) Q_0(\rho) - \tfrac{2}{3} Q_2(\rho) P_2(\rho_1) P_2(\mu)\} d\rho_1 \right.$$
$$\left. + \int_\rho^\infty e^{-\lambda d \rho_1} \{(\rho_1^2 - \tfrac{1}{3}) Q_0(\rho_1) - \tfrac{2}{3} Q_2(\rho_1) P_2(\rho) P_2(\mu)\} d\rho_1 \right].$$

Using the formulae

$$Q_0(\rho) = \log \frac{\rho + 1}{\rho - 1}, \quad Q_2(\rho) = -3\rho + \tfrac{1}{2}(3\rho^2 - 1) \log \frac{\rho + 1}{\rho - 1},$$

together with

$$\int_\rho^\infty e^{-\nu\rho_1} (\rho_1^2 - \tfrac{1}{3}) \log \frac{\rho_1 + 1}{\rho_1 - 1}\, d\rho_1$$
$$= \frac{e^{-\nu\rho}}{\nu^3} \left[(\nu^2\rho^2 + 2\nu\rho + 2 - \tfrac{1}{3}\nu^2) \log \frac{\rho + 1}{\rho - 1} - 2\nu \right]$$
$$+ (2\nu + 2 + \tfrac{2}{3}\nu^2) \frac{e^{-\nu}}{\nu^3} Ei\{-\nu(\rho - 1)\} - (-2\nu + 2 + \tfrac{2}{3}\nu^2) \frac{e^{\nu}}{\nu^3}$$
$$\times Ei\{-\nu(\rho + 1)\},$$

we find

$$I_2 = \frac{2\pi^2 e^2 S d^2}{\lambda^3} \left\{ [1 - P_2(\mu) P_2(\rho)] \right.$$
$$\times \left[-\frac{2e^{-\nu\rho}}{\nu^2} + \frac{2S}{\nu^4} \left(Ei(-\nu\sqrt{\rho - 1}) + \log \frac{\rho + 1}{\rho - 1} \right) - \frac{2S'}{\nu^3} Ei(-\nu\sqrt{\rho + 1}) \right]$$
$$\left. + \frac{6S\rho}{\nu^3} P_2(\mu) - \frac{e^{-\nu\rho}}{\nu^3} P_2(\mu)(6\rho + \sqrt{3\rho^2 + 1}\,\nu) \right\},$$

where $\nu = \lambda d$, $S' = (1 - \nu + \frac{1}{3}\nu^2) e^\nu$.

* *Vide* Y. Sugiura, *Zeit. für Phys.* 45, p. 484 (1927).

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In the symmetrical case considered we have $\rho = 2$, $\mu = 0$, $P_2(\mu) = -\frac{1}{2}$, $P_2(\rho) = \frac{11}{2}$. This gives then

$$I_2 = \frac{2\pi^2 e^2 S}{\lambda^6 d}\,[e^{-2\nu}(6-\nu) + S\{7{\cdot}5\,Ei(-\nu) + 2{\cdot}2\} - 7{\cdot}5\,S'\,Ei(-3\nu)].$$

Again, from (8),

$$J_1 = 2\int\frac{1}{q_1}e^{-2\lambda p_1}\,dv_1\int e^{-\lambda(r_2+q_2)}\,dv_2 + 2\int\frac{1}{q_2}e^{-\lambda(r_2+q_2)}\,dv_2\int e^{-2\lambda p_1}\,dv_1$$

$$= \tfrac{1}{2}I_1 S + \frac{d^3}{4}\frac{\pi}{\lambda^3}\int e^{-\lambda d\rho_2}(\rho_2+\mu_2)\,d\rho_2\,d\mu_2\,d\phi_2$$

$$= \tfrac{1}{2}I_1 S + \frac{2\pi^2}{\lambda^6}(d\lambda^2+\lambda)\,e^{-\lambda d},$$

and (9) gives

$$J_2 = 2\int\frac{1}{q_1}e^{-\lambda(r_1+p_1)}\,dv_1\int e^{-\lambda(p_2+q_2)}\,dv_2 + 2\int\frac{1}{q_2}e^{-\lambda(v_2+q_2)}\,dv_2\int e^{-\lambda(r_1+p_1)}\,dv_1$$

$$= \tfrac{1}{2}I_2 + \frac{2\pi^2}{\lambda^6}Se^{-\lambda d}(d\lambda^2+\lambda).$$

In fig. 1 these expressions are graphed as functions of the nuclear separation. The energy of interaction for the two cases of parallel and antiparallel spins is illustrated in fig. 2. It is quite clear from the curves that the addition of the third proton produces a much

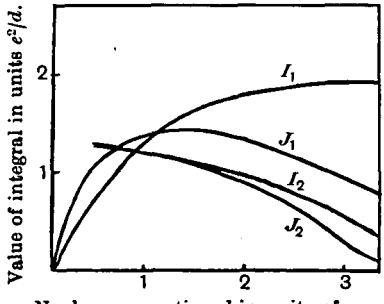


Fig. 1. Illustrating perturbation integrals for H_3^+.

less stable compound with much wider nuclear separation. The equilibrium separation cannot be fixed with any certainty and it is still doubtful whether we must regard H_3^+ as a true homopolar compound or a polarisation compound. It would appear that the electron pair bond is not quite strong enough to hold the extra proton. In fig. 2 is shown also the form of energy curve which would result if a wave function symmetrical in all three nuclei were

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permitted. The comparative instability of the ion must then be regarded as a consequence of proton spin. One must conclude that nuclear symmetry considerations are of considerable importance in the theory of polyatomic molecules with similar nuclei. Thus one would expect from the above calculation that molecules with three equivalent nuclei without nuclear spin, as for example O_3, should be more stable than those with nuclear spin, such as N_3.

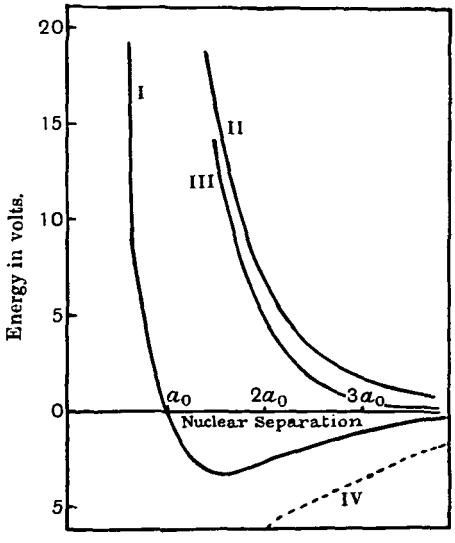


Fig. 2. Energy curve for H_3^+.

I, Energy curve for $1^1\Sigma$ state of H_2; II, Additional energy due to added proton; III, Energy curve for H_3^+; IV, Curve which would be obtained for H_3^+ if a function symmetrical in three protons were allowed.

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