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ABSTRACT

The excitation of an H-atom by an incident monochromatic wave is dealt with using the two-body wave function of the atom. It is shown that this method gives results resembling very strongly the classical results obtained by H. Hertz.

АННОТАЦИЯ

Исследуется Н-атом возбужденный монохроматической волной. Н-атом описывается двойной функцией волны. Показывается, что полученные таким образом результаты очень похожи на классические результаты, полученные Герцем.

KIVONAT

A monokromatikus hullámmal gerjesztett H-atomot vizsgáljuk. A H-atomot kéttest hullámfüggvénnyel irjuk le. Megmutatjuk, hogy az igy kapott eredmények nagyon hasonlitanak a Hertz által kapott klasszikus eredményekhez.

The old theory of Bohr treated the H-atom considering both electron and proton as classical point particles. The wave mechanical treatment replaces the point particles by waves, however, in most of the discussions of the H-atom the nucleus is still taken as point and only the electron is described by a wave function. The latter treatment has its advantage as it leads to quantitatively correct result - in particular if we introduce the effective mass

$$m = \frac{m_1\ m_2}{m_1+m_2}$$

of the electron.

This one-body treatment of the H-atom is justified because of its success, however statement to the effect that "the proton can be treated classically because its mass is so much larger then of electron" must be taken with precaution. Indeed, it follows from the uncertainty relation that a proton confined initially to a region with linear dimension of the order of $r_o = 10^{-12}$ cm would expand so that after 10^{-8} sec it occupies a region with linear dimensions of meters!

The wave mechanical treatment of problems as one-body problem has in fact its strong limitations. We have shown /1/ that treating the Stern-Gerlach effect of H-atoms as one-body problem and supposing the motion of the electron to be described by a wave function $\psi(\underline{r},t)$ and the action of the proton as that of a classical point particle - this treatment leads to the incorrect classical result - i.e. it leads to expect that the atomic beam is being spread out continuously when traversing the inhomogeneous magnetic field. The observed effect is only obtained if we describe the H-atoms by two-body wave functions

$$\Psi(\underline{\underline{r}},t) = \psi(\underline{r}_1\underline{r}_2,t).$$

The above remarks make it worthwhile to investigate the treatment of the H-atom as two-body problem in some detail.

The wave equation of the unperturbed H-atom can be written

$$H_o\psi = i\hbar\dot{\psi}, \qquad /1/$$

where

$$H_o = -\frac{1}{2}\hbar^2 \sum_{\nu=1}^{2} \frac{\nabla_\nu^2}{m_\nu} - \frac{e^2}{|\underline{r}_1-\underline{r}_2|} . \qquad /1a/$$

Stationary solution of /1/ can be obtained in terms of centre of gravity and relative coordinates, i.e.

$$\begin{aligned} \underline{R} &= \alpha_1\underline{r}_1 + \alpha_2\underline{r}_2 \\ \underline{s} &= \underline{r}_1 - \underline{r}_2 \end{aligned} \qquad /2/$$

with

$$\alpha_\nu = \frac{m_\nu}{m_1+m_2}, \qquad \nu=1,2$$

From /2/ it follows also

$$\begin{aligned} \underline{r}_1 &= \underline{R} + \alpha_2\,\underline{s} \\ \underline{r}_2 &= \underline{R} - \alpha_1\,\underline{s} \end{aligned} \qquad /3/$$

and

$$d^6\underline{\underline{r}} = d^3\underline{r}_1 d^3\underline{r}_2 = d^3\underline{R}\, d^3\underline{s} .$$

The stationary solutions of /1/ can thus be written

$$\psi_{n\ell}\,(\underline{\underline{r}},t) = \Phi_{n\ell}e^{-i\omega_{n\ell}t}$$

and /4/

$$\phi_{n\ell} = \frac{1}{L^{3/2}}\, e^{i\underline{K}_\ell\underline{R}}\varphi_n\,(\underline{s}), \qquad \omega_{n\ell}=\omega_n + \frac{\hbar\, K_\ell^2}{2\,(m_1+m_2)}$$

where φ_n $(\underline{s})$ are eigenfunctions and ω_n the eigenfrequencies of the one-body problem /with reduced mass/.

Further

$$\underline{K}_\ell = \frac{2\pi\underline{\ell}}{L}, \qquad /5/$$

where $\underline{\ell}$ are vectors the components of which are integers.

We note, that /1/ possesses no stationary solutions which can be normalized. However, if we take the H-atom to be enclosed into a cubic box with side length L, then we can suppose the stationary solutions inside this box to be given in a good approximation by /4/. Strictly certain small corrections in the vicinity of the walls should be applied, we neglect these corrections.

The functions $\underline{\Phi}_{n\ell}$ form a complete orthogonal set of functions in terms of which arbitrary functions of $\underline{\underline{r}}$ can be developed inside the box.

Considering an electromagnetic plane wave falling on the H-atom enclosed into the box, the vector potential of the incident wave can be written.

$$\underline{A}\ (\underline{r},t) = \frac{1}{2}\underline{A}_o e^{i(\underline{Kr} - \Omega t)} + c.c. \qquad /6/$$

respectively

$$\underline{A}_\nu = \frac{1}{2}\underline{A}_o\left[e^{i(\underline{K}\cdot\underline{r}_\nu - \Omega t)} + e^{-i(\underline{K}\,\underline{r}_\nu - \Omega t)}\right].$$

The effect of the electromagnetic wave can be described by a perturbation operator P and thus the perturbed atom obeys the wave function

$$(H_o + P)\ \psi = i\hbar\psi' \qquad /7/$$

where

$$P = P^+e^{-i\Omega t} + P^-e^{i\Omega t}, \qquad /8/$$

with $P^+ = \sum_{\nu=1}^{2} P^+_\nu$ and $P^- = \sum_{\nu=1}^{2} P^-_\nu$

Thus the perturbation consists of four terms corresponding to the actions of the wave on the electron and on the proton $/\nu = 1,2/$ and also corresponding to the frequencies $\pm\Omega$ of the electromagnetic wave. We have explicitly

$$P^\pm_\nu = i\beta_\nu \underline{A}_o e^{\pm i\underline{Kr}_\nu} \,\mathrm{grad}_\nu \qquad /9/$$

with $\beta_\nu = \dfrac{e_\nu\hbar}{2m_\nu c}$ and $e_1 = -e_2$ = charge of the electron. We have neglected here terms in $\underline{A}^2$. The solution of /7/ corresponding to a state

$$\underline{A}_o = 0$$

can be written as

$$\psi_{n_o\ell_o} = \phi_{n_o\ell_o} e^{-i\omega_{n_o\ell_o} t}, \qquad /10a/$$

where

$$\phi_{n_o\ell_o} = \frac{1}{L^{3/2}} e^{i \underline{K}_o \underline{R}} \varphi_o (\underline{s}), \qquad /10b/$$

and

$$\omega_{n_o\ell_o} = \omega_o . \qquad /10c/$$

Thus the perturbed solution can be written when neglecting terms of higher order in $\underline{A}_o$

$$\psi = \phi_{n_o\ell_o} e^{-i\omega_o t} + a^+ e^{-i(\omega_o+\Omega)t} + a^- e^{-i(\omega_o-\Omega)t} . \qquad /10/$$

Inserting /10/ into /7/ we obtain differential equations for $a^{\pm}$. Developing the latter quantities in terms of the eigenfunctions $\phi_{n\ell}$ we can write

$$a^{\pm} = \sum c^{\pm}_{n\ell} \phi_{n\ell} \qquad /11/$$

where

$$c^{\pm}_{n\ell} = \frac{\int \phi^*_{n\ell}\, P^{\pm} \phi_{n_o\ell_o}\, d^6\underline{\underline{r}}}{L^3 \hbar\, (\omega_o - \omega_{n\ell} \pm \Omega)} \qquad /12/$$

The integrals in the denominators of /12/ can be worked out in a straightforward manner and thus we obtain the perturbation of the wave function by the incident electromagnetic wave.
Let us write

$$\underline{p}^{\pm}_{\nu n\ell} = \int \phi^*_{n\ell}\, e^{\pm i \underline{K}\underline{r}_\nu} \mathrm{grad}_\nu\, \phi_{n_o\ell_o}\, d^6\underline{\underline{r}} \qquad /13/$$

thus

$$c^{\pm}_{n\ell} = \frac{i(\beta_1 \underline{p}^{\pm}_{1n\ell} + \beta_2\, \underline{p}^{\pm}_{2n\ell})\underline{A}_o}{L^3 \hbar\, (\omega_o - \omega_{n\ell} \pm \Omega)} \qquad /14/$$

The integral on the right side of /13/ can be transformed into one with variables $\underline{R}'$, $\underline{s}'$. By using /3/ we have

$$\mathrm{grad}_{\underline{r}_1} = \alpha_1 \frac{\partial}{\partial \underline{R}} + \frac{\partial}{\partial \underline{s}} \quad \text{and} \quad \mathrm{grad}_{\underline{r}_2} = \alpha_2 \frac{\partial}{\partial \underline{R}} - \frac{\partial}{\partial \underline{s}} .$$

As can be seen at once the integrations over s' give two kinds of terms of the form

$$\int \varphi_n^* (\underline{s}') \, \varphi_o (\underline{s}') e^{\pm i\alpha_\nu (\underline{K}\,\underline{s}')} d^3\underline{s} \approx 0 \qquad /15a/$$

and

$$\int \varphi_n^* (\underline{s}') \, \mathrm{grad}_{\underline{s}'} \, \varphi_o (\underline{s}') e^{\pm i\alpha_\nu} (\underline{K}\,\underline{s}') d^3\underline{s} \approx \underline{p}_n , \qquad /15b/$$

where

$$\underline{p}_n = \int \varphi_n^* (\underline{s}') \, \mathrm{grad} \, \varphi_o (\underline{s}') d^3\underline{s}' \qquad /16/$$

is proportional to the dipol moment of the mixed state with components φ_o and φ_n.

The approximations /15/ are valid if we consider $\exp(i\alpha_2 \underline{Ks})$ to be a function which varies very slowly as compared with $\varphi_o(\underline{s})$ or $\varphi_n(\underline{s})$. The latter assumption implies that

$$\lambda >> r_H$$

i.e. the wave length λ of the incident beam is large as compared with the Bohr radius r_H. Inserting /15/ into /13/ we find

$$\underline{p}^{\pm}_{\nu,n\ell} = (-1)^{\nu+1} \underline{p}_n \frac{1}{L^3} \int e^{i[(\underline{K}_o - \underline{K}_\ell) \pm \underline{K}]\underline{R}'} d^3\underline{R}' \qquad /17/$$

Inserting /17/ into /14/ and neglecting the dependence of $\omega_{n\ell}$ on ℓ and thus writing $\omega_{n\ell} \sim \omega_n$ we obtain

$$c^{\pm}_{n\ell} = \frac{i\beta}{L^6} \frac{\underline{A}_o \, \underline{p}_n}{\omega_o - \omega_n \pm \Omega} \int e^{i[(\underline{K}_o - \underline{K}_\ell) \pm \underline{K}]\underline{R}} d^3\underline{R} \qquad /18/$$

where $\beta = \frac{e}{2mc}$

The summation of ℓ in /11/ can be carried out in a good approximation. We may write

$$\sum_\ell e^{-i\underline{K}_\ell (\underline{R}' - \underline{R})} = L^3 \delta(\underline{R}' - \underline{R})$$

and thus

$$\sum_{\ell} e^{i\underline{K}_{\ell}\underline{R}} \int e^{i[(\underline{K}_o-\underline{K}_{\ell})\pm K]\underline{R}'} d^3\underline{R}'=L^3 e^{i(\underline{K}_o\pm\underline{K})\underline{R}}$$

we find thus that

$$a^{\pm} = i\frac{\beta}{L^{9/2}} \sum_n \frac{(\underline{A}_o\underline{p}_n)\varphi_n(\underline{s})}{\omega_o-\omega_n\pm\Omega} e^{i(\underline{K}_o\pm\underline{K})\underline{R}} \qquad /19/$$

We can write as a good approximation

$$a^{\pm} = e^{i(\underline{K}_o\pm\underline{K})\underline{R}} \sum c_n^{\pm} \varphi_n(\underline{s}) \qquad /20/$$

where

$$c_n^{\pm} = \frac{i\beta}{L^{9/2}} \frac{1}{\omega_o-\omega_n\pm\Omega} (\underline{A}_o\underline{p}_n) \qquad /20a/$$

It is apparent that the terms in /14/ correspond to various wave numbers $\underline{K}_{\ell}$ but the sum of these terms gives in form of a Fourier synthesis terms with wave number $\underline{K}$ of the incident radiation.

Thus from /20/, /10/ and /10b/ we get for the wave function of an H-atom perturbed by a monochromatic wave

$$\psi = (\phi_o+b^+(\underline{s})e^{i(\underline{KR}-\Omega t)} +b^-(\underline{s})e^{-i(\underline{KR}-\Omega t)})e^{i(\underline{K}_o\underline{R}-\omega_o t)} \qquad /21/$$

where

$$\phi_o = \frac{1}{L^{3/2}} \varphi_o(\underline{s})$$

and

$$b^{\pm}(\underline{s}) = \sum_{n\neq o} c_n^{\pm} \varphi_n(\underline{s}).$$

/for $c_n^{\pm}$ see /20a/ /.

The electron density can be obtained by integrating $\psi^*\psi$ over the proton coordinate

$$\rho_1(\underline{r}) = \int \psi^*\psi d^3\underline{r}_2\Big|_{\underline{r}_1=\underline{r}} \qquad /22/$$

Similarly the electron current density

$$\underline{i}_1(\underline{r}) = -i\beta_1 \int (\psi^* \mathrm{grad}_1 \psi - \psi \mathrm{grad}_1 \psi^*) d^3\underline{r}_2 \Big|_{\underline{r}_1=\underline{r}} - \frac{e^2}{m_1 c^2} \int \underline{A}(\underline{r}_1)\psi^*\psi d^3\underline{r}_2 \Big|_{\underline{r}_1=\underline{r}} \qquad /23/$$

Introducing /21/ into /22/ and /23/ we obtain terms proportional to the following integrals

$$\left.\begin{aligned} D_{on} &= \int \varphi_o^*(\underline{s})\varphi_n(\underline{s}) e^{\pm i\underline{KR}}\, d^3\underline{r}_2 \Big|_{\underline{r}_1=\underline{r}} \\ &\text{and} \\ I_{on} &= \int \varphi_o^*(\underline{s}) \mathrm{grad}_{\underline{r}_1} (\varphi_n(\underline{s}) e^{\pm i\underline{KR}}) d^3\underline{r}_2 \Big|_{\underline{r}_1=\underline{r}}. \end{aligned}\right\} \qquad /24/$$

The latter integrals can be worked out in a good approximation if we change the integration into $\underline{s}$ and put

$$\underline{R} = \underline{r}_1 - \alpha_2 \underline{s} \qquad \text{and} \qquad d^3\underline{r}_2 = -d^3\underline{s}.$$

We thus get

$$D_{on} = e^{i\underline{kr}} \int \varphi_o^*(\underline{s})\varphi_n(\underline{s}) e^{\pm i\alpha_2 \underline{Ks}}\, d^3\underline{s}$$

and as we have shown already in connection with /15a/

$$D_{on} = 0.$$

Similarly, since from /2/

$$\mathrm{grad}_{\underline{r}_1} = \alpha_1 \mathrm{grad}_{\underline{R}} + \mathrm{grad}_{\underline{s}}$$

we have

$$\mathrm{grad}_{\underline{r}_1}(e^{i\underline{KR}}\varphi_n(\underline{s})) = (i\underline{K}\alpha_1\varphi_n(\underline{s}) + \mathrm{grad}_{\underline{s}}\varphi_n(\underline{s}))e^{i\,\underline{KR}}$$

and thus in the same approximation as /15b/ we have

$$I_{on} = e^{\,i\underline{Kr}}\,\underline{p}_n.$$

/ $\underline{p}_n$ is given in /16/ /.

We find in a good approximation

$$\rho_1^p(\underline{r}) = -e\rho_1(\underline{r}) = \frac{e}{L^3}, \qquad /25/$$

and

$$\underline{i}_1(\underline{r}) = \frac{e}{m_1 c^2}\,\rho_1^e(\underline{r})\underline{A}(\underline{r})\kappa \qquad /26/$$

where

$$\kappa = 1 + \frac{4}{L^3 m}\sum \frac{E_o - E_n}{(\omega_o - \omega_n)^2 - \Omega^2}\; p_n^2 \qquad /26a/$$

with $E_o = \hbar\omega_o$, $E_n = \hbar\omega_n$

The electromagnetic field propagated inside the box satisfies the electromagnetic wave equation, i.e.

$$\nabla^2\underline{A} - \frac{1}{c^2}\ddot{\underline{A}} = -\,4\pi\underline{i}_1(\underline{r}). \qquad /27/$$

In this way we obtain from the perturbation calculations of the two--body wave function the results obtained by H.Hertz from classical considerations. The new feature of the wavemechanical treatment is that the "oscillation strength" introduced by Hertz can be calculated from the perturbation matrices.

The interesting feature of the consideration is, however, that while the one-body treatment makes to appear the classical considerations only qualitatively correct - the two-body treatment leads exactly to the classical result obtained from the model of the "harmonically bound electrons".

It is interesting to extend the above consideration to cases where the density $\rho_1(\underline{r}) \neq$ constant. The simplest case is a state which is a superposition of states corresponding to atoms with translational motions, thus we may put

$$\Psi = \sum_\nu \gamma_\nu e^{i(\underline{K}_{o\nu}\underline{R} - \omega_{o\nu}t)}\psi, \qquad /28/$$

where

$$\omega_{o\nu} = \frac{\hbar\kappa_{o\nu}^2}{M},$$

with $M = m_1 + m_2$

Indeed, /28/ satisfies the perturbed wave equation if small terms are neglected - the latter are due to the fact, that the effective frequency acting on the moving atoms differs from Ω by the Doppler shift corresponding to their translational velocities.

Working out the electron density corresponding to the mixed state, we find using the method above that

$$\dot{\rho}_1(\underline{r}) = \int \Psi^* \Psi d^3\underline{r}_2 \Big|_{\underline{r}_1=\underline{r}} = \frac{1}{L^3} \sum_{\nu,\mu} \gamma_\nu \gamma_\mu^* \exp\left\{i\left[(\underline{K}_{o\nu} - \underline{K}_{o\mu} - \underline{K})\underline{r} + (\omega_{o\nu} - \omega_{o\mu} - \Omega)t\right]\right\}$$

The latter density shows strongly fluctuations in space and oscillations with frequencies around Ω . /If we take the $K_{o\nu}$ as wave numbers of thermal velocities then we can suppose $K_{o\nu} \sim K$ to appear in the thermal spectrum, nevertheless because of the large mass of the H-atoms $\omega_{o\nu} \ll \Omega$ /. Thus the frequencies appearing in the spectrum correspond to the original frequency Ω with Doppler broadening.

Indeed, if we have for a particular value of ν

$$K_\nu \sim K$$

thus

$$\omega_\nu \approx \frac{\hbar K^2}{M} = \frac{\hbar\Omega}{M c^2} \Omega \ll \Omega$$

Since $\hbar\Omega/Mc^2$ is the ratio of the energies of the incident photons and the rest energies of the H-atoms.

The current intensity of the electrons in the mixed state is obtained similarly. Using the formalism explicitly for the state we find for the electron of the mixed state /neglecting Doppler shifts/

$$\bar{\underline{i}}_1(\underline{r}) = \frac{e^2}{Mc^2} \bar{\rho}_1(\underline{r})\underline{A}(\underline{r})\kappa$$

where κ has the same value as before. We see therefore that the incident wave produces oscillations with current densities equal to that obtained by the classical theory even in the case where the atomic state is not a stationary one but shows fluctuations of density.

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