the $S_{i\kappa}\varepsilon_j$ by comparison with β. I show here that this is not so.

Consider combined orbitals of the following form instead of the ordinary ones:

$$\varphi_i^c = \sum_\kappa R_{i\kappa}\,\varphi_\kappa, \tag{4}$$

in which the φ_κ are basic functions and

$$R_{i\kappa} = \sum_\alpha (1 - S_{i\alpha})\,P_{\alpha\kappa}, \tag{5}$$

in which the $P_{\alpha\kappa}$ are elements of the coupling matrix defined by

$$P_{\alpha\kappa} = \sum_i c_{\alpha j}\,c_{i\kappa}^{+}. \tag{6}$$

Then to an accuracy of S^2 we may assume that the basis is orthogonal, and, as has been shown [2], the energy may be put as

$$E = \sum_\kappa \langle\, \varphi_\kappa^{c+} \hat{F}\,\varphi_\kappa \,\rangle\ . \tag{7}$$

Variation with respect to (6) subject to the additional condition $\int \varphi_i\,\varphi_\kappa\, d\tau = S_{i\kappa}$ then gives

$$\det|\,F_{i\kappa} - \varepsilon_j\delta_{i\kappa}^2\,| = 0. \tag{8}$$

The form of the $F_{i\kappa}$ coincides with Mulliken's formulas, so that $S_{i\kappa}$ of (2) should be replaced by the $\delta_{i\kappa}$ if we calculate the $\beta_{i\kappa}$ in accordance with [1]. The semiempirical approximation of [1] may thus be justified via the use of combined orbitals, so its use in [1] is in order.

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Kuznetsov Siberian Institute of Technical Physics

A VARIATION PRINCIPLE IN THE DYNAMIC SCATTERING OF X-RAYS

V. S. Mospanov

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Consider the scattering of x-rays by an ideal crystal whose nuclei are rigidly fixed. We then have to consider the interaction with the crystal as a whole, because we have to solve Maxwell's equation for the vector potential A jointly with Schrödinger's equation for the crystal:

$$\left.\begin{aligned} \Delta A - \frac{1}{c^2}\ddot{A} &= \frac{4\pi}{c} J \\ (H_0 + H_{\text{in}})\,\Psi &= ih\dot{\Psi}, \end{aligned}\right\} \tag{1}$$

in which J is the current representing the reaction of the crystal on the radiation

$$J = \int \Psi^* \hat{j}\,\Psi\, d\tau, \tag{2}$$

$$\hat{j} = \frac{ich}{2m}\sum_\alpha (\nabla_\alpha\,\delta(r - r_\alpha) + \delta(r - r_\alpha)\,\nabla_\alpha) + \frac{e^2}{mc}\sum_\alpha \delta(r - r_\alpha)\,A(r, t). \tag{3}$$

We substitute (3) into (2) and introduce the microscopic (unaveraged) density $\rho(r)$ to get

$$J(r, t) = \frac{ich}{2m}\int \sum_\alpha \psi^*\,[\nabla_\alpha\,\delta(r - r_\alpha) + \delta(r - r_\alpha)\,\nabla_\alpha]\,\psi d\tau + \frac{e\rho(r)\,A(r, t)}{mc}. \tag{4}$$

The first term in (4) is of importance in resonant scattering of γ-rays; it will be considered elsewhere. Resonance effects are unimportant in x-ray scattering, so this term may be neglected and (1) may be replaced by

$$\Delta A - \frac{1}{c^2}\ddot{A} = \frac{4\pi e \rho(r) A}{mc^2}. \tag{5}$$

Taking A(t) as harmonic, we reduce (5) to

$$\Delta A + \kappa^2 A = \frac{4\pi e}{mc^2}\rho(r) A(r). \tag{6}$$

Equation (6) is easier to solve than the usual equation in Laue's dynamical theory [1]; it may be formulated as a variational principle, for which purpose we transfer from the differential form of (6) to an integral one:

$$A(r) = \frac{4\pi e}{mc^2}\int G(r, r')\rho(r') A(r')\, d\tau'. \tag{7}$$

The Green's function G(r, r') satisfies

$$\Delta G + \kappa^2 G = \delta(r - r') \tag{8}$$

and the condition of periodicity $G(r + a, r') = e^{i\kappa a}G(r, r')$. The periodicity in the density also causes A to be periodic, the repeat distance being that of the lattice:

$$A(r + a) = e^{i\kappa a} A(r). \tag{9}$$

It is then sufficient to find $A_0(r)$ for a single cell. For the whole crystal

$$A(r) = \sum_{e} e^{i\kappa r_l} A_0(r - r_l). \tag{10}$$

The integral equation (7) corresponds to a variational principle [2, 3]:

$$\delta\Lambda = 0, \tag{11}$$

$$\Lambda = \frac{4\pi e^2}{mc^2}\int A^*(r)\rho(r)A(r)\,d\tau - \left(\frac{4\pi e}{mc^2}\right)^2\int A^*(r)\rho(r)G(r, r')A(r')\rho(r')\,d\tau\,d\tau'. \tag{12}$$

We replace the cell by the equivalent sphere of radius R and use (6) to eliminate $\rho(r)$ from (12):

$$\Lambda = \lim_{\varepsilon\to 0}\Lambda_\varepsilon, \tag{13}$$

$$\Lambda_\varepsilon = \int\limits_{r<R-2\varepsilon} ds \int\limits_{r'<R-\varepsilon} ds' \left[\frac{\partial A^*}{\partial r} - A^*\frac{\partial}{\partial r}\right]\left[A\frac{\partial}{\partial r'}G(r, r') - G(r, r')\frac{\partial A}{\partial r'}\right]. \tag{14}$$

The solution is found by expanding A and G with respect to the spherical harmonics of (2); the trial functions are of the form

$$A_n(r) = \sum_{l=0}^{l=n}\sum_{m} C_{lm} R_l(r) Y_{lm}(\vartheta, \varphi). \tag{15}$$

$R_l(r)$ satisfies

$$\left[\frac{d^2}{dr^2} + \kappa^2 - \frac{4\pi e\rho(r)}{mc^2} - \frac{l(l+1)}{r^2}\right] rR_l(r) = 0. \tag{16}$$

The expansion in Laue's method employs plane waves, whereas the present solution takes account of the translational symmetry and gives an expansion in spherical harmonics.

Consider the case $l = 0$; the trial function is $A_0 = CR_0(r)$, in which $R_0(r)$ satisfies

$$\left[\frac{d^2}{dr^2} + \kappa^2 - \frac{4\pi e\rho(r)}{mc^2}\right] r R_0(r) = 0. \tag{17}$$

The solution is essentially dependent on the form of $\rho(r)$; for point scattering we may transform (17) to

$$\left[\frac{d^2}{dr^2} + \kappa^2 - \frac{4\pi e^2 N_0 F}{mc^2}\right] r R_0(r) = 0,$$

in which F is the structure factor. The solution is $R_0 = e^{i\varkappa r}/i\varkappa r$, with $\varkappa = \sqrt{\kappa^2 - 4\pi e2N_0F/mc^2}$. If $\kappa^2 \gg 4\pi e^2N_0F/mc^2$, then $\varkappa = \kappa - 2\pi e^2N_0F/\kappa mc^2$, i.e., allowance for the interaction causes an additional phase change. If $\rho(r) = c/r^{\alpha}(\alpha \gtrsim 1)$, we get attenuation not associated with absorption, namely primary extinction.

This method is convenient when the radiation arises within the crystal.

I am indebted to Dr. D. F. Zaretskii for direction in this work.

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Moscow Institute of Engineering Physics

ION DIFFRACTION IN ELECTROLYTES*

V. I. Vashchuk

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A recent paper [1] describes an experiment whose result the workers interpreted as diffraction of Cu^{2+} ions in aqueous $CuSO_4$ during electrolysis. This interpretation conflicts with the generally accepted position that quantum effects become important when the De Broglie wavelength of the atoms becomes comparable with the interatomic distances [2]. This is obviously not the case for electrolytes.

The description itself forces us to reject the interpretation, for ions diffracted at a hole 0.2-2 mm from the cathode and moving at 10^{-3} cm/sec would take 20-200 sec to reach the cathode, whereas the electrolysis is run for only 10 sec. It is stated that longer times do not produce a normal diffraction pattern. It is clear that the cathode receives ions already very close to it; no diffraction at the hole is observable.

The screen with a hole in it acts by perturbing the electric field between the plates; the polarization near the cathode gives the field the form shown in Fig. 1.

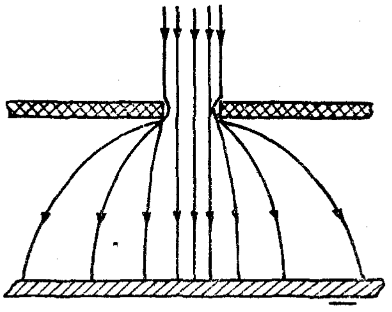

Fig. 1

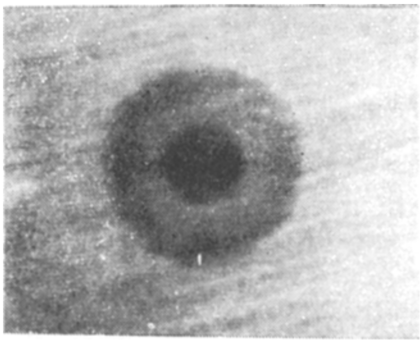

Fig. 2

No ions pass through the hole if this is closed with a metal foil, but the electric field is unaltered. I have tried this and have found that the pattern is the same and is obtained as readily as when the hole is open (Fig. 2). This again shows that the wave aspect of the ions has no part in producing the pattern.

It also follows that the hole could be replaced by a circular rod with one end near the cathod to give precisely the same pattern, as one would expect, because the electric field is then the same as for the screen with a hole.

I have found that an unchanged pattern is obtained if this rod has the same diameter as the hole in the screen and has its end the same distance away. The deposition of the copper is dependent on the distance between rod and cathode for a given mean electric field U/r, but there is none of the alternation of central maxima and minima to be expected from diffraction or interference. There is merely a gradual weakening of the central dark spot, which vanishes (minimum) with increase in distance but is not replaced by any subsequent maximum.

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*Shortened version of the original.