

Symmetry Requirements in Electron Scattering by an Atom

L. E. H. TRAINOR* AND TA-YOU WU
 Division of Physics, National Research Council, Ottawa, Canada
 (Received September 15, 1952)

It is pointed out that in the treatment of the problem of electron scattering by an atom including the effect of the Pauli principle, the use of unsymmetrized wave function and asymptotic conditions in one electron does not ensure the required asymptotic conditions in the other electron. However, the use of symmetrized wave functions automatically ensures symmetrical asymptotic conditions in both electrons.

IN a recent note¹ the treatment of electron scattering by hydrogen-like atoms by Mott and Massey² is discussed. At the end of the second section, the possibility of simultaneously satisfying the symmetry requirements and the asymptotic conditions as they are stated by Mott and Massey is questioned. The purpose of the present note is to point out that the implication of symmetrized wave functions in their treatment insures symmetrized asymptotic conditions, and hence, their scheme is consistent from the point of view of symmetry requirements.

Since the Hamiltonian of the system under discussion is symmetric in the two electrons, it is evident that if a set of asymptotic conditions uniquely determines a solution of the Schrödinger equation, then the solution so determined has the same symmetry properties as are expressed in the asymptotic conditions. Conversely, if one assumes symmetrized solutions, one implies symmetrized asymptotic conditions. The treatment of Mott and Massey serves as an illustration.

Let $\Psi(1, 2)$ be any solution whatsoever of the Schrödinger equation for the two-electron atomic system, and let it be expanded as a function of the coordinates of one electron in terms of the complete set of hydrogenic functions,

$$\Psi(1, 2) = \sum \varphi_n(1) \Phi_n(2), \quad (1)$$

where the expansion coefficients Φ_n are functions of the coordinates of the second electron. On substitution of (1) into the Schrödinger equation, one obtains

$$(\Delta_2 + k_n^2) \Phi_n(2) = \int \varphi_n^*(1) \left[-\frac{2z}{r_2} + \frac{2}{r_{12}} \right] \Psi(1, 2) dx_1, \quad (2)$$

which is an infinite system of differential equations. If one requires the asymptotic conditions

$$\begin{aligned} \Phi_n(2) \rightarrow \delta_{n0} e^{ik_n r_2} + \frac{e^{ik_n r_2}}{r_2} \xi_n(\vartheta_2, \varphi_2), \quad k_n^2 > 0, \\ \rightarrow \text{exponentially decreasing} \quad k_n^2 < 0, \\ \text{function of } r_2, \end{aligned} \quad (3)$$

* National Research Laboratories Post-doctoral Fellow, now at Queens University, Kingston, Ontario, Canada.

¹ T. Y. Wu, Phys. Rev. **87**, 1012 (1952).

² N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, London, 1949), pp. 140, 215, 258.

the system (2) can be put in the form

$$\begin{aligned} \Psi(1, 2) = \varphi_0(1) e^{ik_0 \cdot r_2} \\ + \sum \int \varphi_n(1) \int \int \frac{\exp(ik_n |r_2 - r_2'|)}{4\pi |r_2 - r_2'|} \\ \times \varphi_n^*(1') \left[-\frac{2z}{r_2'} + \frac{2}{r_{12}'} \right] \Psi(1', 2') dx_1' dx_2'. \quad (4) \end{aligned}$$

It is generally assumed that the conditions (3) uniquely determine the solution $\Psi(1, 2)$. In this case, namely, if $\Psi(1, 2)$ in (1) is any solution not necessarily symmetrized, there is no assurance of an asymptotic form corresponding to outgoing waves of electron 1 in the alternative expansion

$$\Psi(1, 2) = \sum \int \varphi_n(2) \chi_n(1).$$

In the particular case in which $\Psi(1, 2)$ is required to be a symmetrized solution, let

$$\begin{aligned} \Psi^\pm(1, 2) = \sum \int [\varphi_n(1) F_n(2) \pm \varphi_n(2) F_n(1)], \\ = \sum \int [\varphi_n(1) F_n(2) \pm \varphi_n(1) G_n(2)], \\ = \sum \int \varphi_n(1) \Phi_n^\pm(2) = \pm \sum \int \varphi_n(2) \Phi_n^\pm(1). \quad (5) \end{aligned}$$

It is evident from (5) that the asymptotic conditions (3) now apply to the coordinates of both electrons in a symmetrical manner, and are expressed in the "solution" (4)³ by virtue of the symmetrized function $\Psi^\pm(1', 2')$ in the integrand.

This theory is satisfactory, except that, in view of the form of the asymptotic conditions (3) imposed, no allowance has been made for finding the cross sections corresponding either to both electrons being ejected into definite directions, or to both electrons being left in a doubly excited state of the two-electron system, i.e., the

³ In the sense of a solution of the integral equation, by iteration, for example.

inverse Auger or auto-ionization transition. In the case of electron scattering by the hydrogen atom, this corresponds to a doubly excited state of the negative hydrogen ion which can undergo auto-ionization.

In actual calculations, one usually replaces $\Psi^\pm(1, 2)$ in the integrand of (4) by the single term corresponding to one electron in the atom and an incident plane wave

(Oppenheimer approximation), or by a finite number of terms from (5).^{1,4} In either case, the use of symmetrized approximation wave functions in (4) implies symmetrized asymptotic conditions in the manner discussed above.

⁴ G. A. Erskine and H. S. W. Massey, Proc. Roy. Soc. (London) **A212**, 512 (1952).

Luminescence and Photoconductivity in Cadmium Sulfide at the Absorption Edge

CLIFFORD C. KLICK

Crystal Branch, Metallurgy Division, Naval Research Laboratory, Washington, D. C.

(Received August 4, 1952)

Measurements of optical transmission, photoconductive response, luminescent edge emission, and excitation spectrum for edge emission have been made on single crystal specimens of CdS at 77°K and 4°K. At the lowest temperature there is an energy gap of more than 0.1 electron volt between the absorption edge and the onset of emission. Coupled with information from the emission spectrum and the infrared properties of CdS, this observation suggests that edge emission in this material may occur at a special center and not be characteristic of the pure lattice.

INTRODUCTION

LUMINESCENT edge emission occurs in cadmium sulfide at the long wavelength side of the absorption edge when the material is cooled to liquid nitrogen temperature (77°K) and excited with ultraviolet light.¹ At liquid helium temperatures (4°K) the emission spectrum of single crystal materials sharpens into a series of equally spaced "lines" with a width at half-maximum of approximately 10Å.² This luminescent emission is less broad than that of impurity activated materials with the exception of activators, such as the rare earths, in which the electronic transition occurs in an inner electronic shell.² One explanation is that either free

electrons and holes or excitons recombine in the pure lattice so that this emission is "lattice" emission. The successive luminescent peaks would correspond to the excitation of increasing numbers of vibrational quanta, and the spacing of the peaks would correspond in energy to the principal infrared vibrational frequency. This simple explanation faces theoretical objections since the probability of electron-hole or exciton recombination in the pure material is relatively small.

The experiments on the electrical and optical properties of CdS at the absorption edge was undertaken primarily to investigate whether edge luminescence was characteristic of the pure lattice. Also, since the large photoconductivity in CdS is technically and scientifically of great interest,³ it was felt that the measurements would aid in understanding this phenomenon. Finally, an understanding of edge emission in CdS might suggest explanations of edge emission in such varied materials as the silver halides⁴ and germanium.⁵

EXPERIMENTAL ARRANGEMENT

The cadmium sulfide investigated here was single crystal material grown from the vapor by the Frerichs technique.⁶ Photoconductivity was measured on a rod-like specimen approximately 1 mm in diameter and 4 mm long. The other measurements were on thin flaked specimens approximately 4 mm×1 mm×0.1 mm. For the emission and excitation measurements the samples were held between quartz plates. Because of this, the

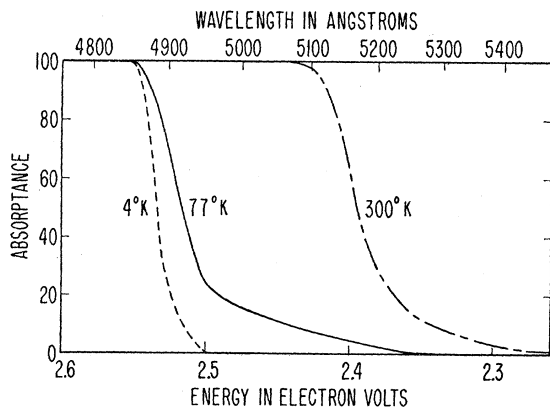


FIG. 1. Absorbance (100 minus percent transmission) of CdS as a function of wavelength for temperatures of 4°K, 77°K, and 300°K. The sample is approximately 0.004 cm thick.

¹ F. A. Kröger, *Physica* **7**, 1 (1940).

² C. C. Klick, *J. Opt. Soc. Am.* **41**, 816 (1951).

³ See, for instance, A. Rose, *RCA Rev.* **12**, 362 (1951) for an introduction to this subject.

⁴ Farnell, Burton, and Hallama, *Phil. Mag.* **41**, 157 (1950).

⁵ J. R. Haynes and H. B. Briggs, *Phys. Rev.* **86**, 647 (1952).

⁶ R. Frerichs, *Naturwiss.* **33**, 381 (1946).