

A Solution of the Schrödinger Equation by a Perturbation of the Boundary Conditions

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A perturbation method is developed which allows a simple calculation of the eigenvalues of the Schrödinger equation by a slight change in the boundary condition.

§1

IN recent years the solution of the Schrödinger equation with a boundary condition at the surface of a finite space has become of some importance. In Wigner and Seitz' theory of metallic wave functions,¹ for instance, $\partial\psi/\partial r$ must vanish at the surface of a sphere. An example with the boundary condition $\psi=0$ at the surface of a sphere was given by Sommerfeld and Welker.² In most of these problems we want to calculate the eigenvalue E as a function of certain parameters which determine the boundary conditions. In the above examples, for instance, we want E as a function of the radius of the sphere. Now let us assume that we have solved the Schrödinger equation for a given radius r_0 . Then, one should imagine that a calculation of the eigenvalue for a somewhat different radius r_0' is possible by means of a perturbation method without giving an exact solution of the Schrödinger equation for this new boundary condition. The ordinary Schrödinger perturbation method cannot be used in the present case, since we do not deal with a perturbation of the potential, but with a perturbation of the boundary condition. We therefore have to find a different method. The special case of metallic wave functions has been already treated in a previous paper.³ In the following we want to describe a more general method⁴ for the solution of the Schrödinger equation by a perturbation of the boundary condition.

§2.

Let E_0 be a nondegenerate eigenvalue and ψ_0 the wave function, satisfying the Schrödinger

¹Wigner and Seitz, *Phys. Rev.* **46**, 509 (1934).
²Sommerfeld and Welker, *Ann. d. Physik* **32**, 56 (1938).
³H. Froehlich, *Proc. Roy. Soc.* **58**, 97 (1936); and *Elektronentheorie der Metalle* (Berlin 1936), p. 272. Cf. also the discussion by Bardeen, *J. Chem. Phys.* **6**, 372 (1938).
⁴A different method was proposed by L. Brillouin, *Comptes rendus* **204**, 1863 (1938).

equation (we use atomic units)

$$\Delta\psi_0 + (E_0 - V)\psi_0 = 0 \quad (1)$$

with a certain boundary condition at the surface S_0 . The wave function ψ_0 can be chosen as a real function since E_0 is not degenerate. We want to calculate the eigenvalue $E = E_0 + \epsilon$ satisfying the Schrödinger equation

$$\Delta\psi + (E_0 + \epsilon - V)\psi = 0 \quad (2)$$

with a slightly different boundary condition at a slightly different surface⁵ S .

We multiply Eq. (1) with ψ and (2) with ψ_0 and subtract both equations. We then find after integration over the space bounded by S with the use of Green's theorem:

$$\int_S \left(\psi_0 \frac{\partial\psi}{\partial n} - \psi \frac{\partial\psi_0}{\partial n} \right) d\sigma + \epsilon \int \psi_0 \psi d\tau = 0. \quad (3)$$

$d\sigma$ means integration over the surface S ; n is the normal to S in the outward direction. We shall consider the following four boundary conditions:

$$A: \quad \psi_0 = 0 \text{ at } S_0, \quad \psi = 0 \text{ at } S \quad (4a)$$

$$B: \quad \psi_0 = 0 \text{ at } S_0, \quad \psi = \mu F \text{ at } S, \quad S = S_0 \quad (4b)$$

$$C: \quad \partial\psi_0/\partial n = 0 \text{ at } S_0, \quad \partial\psi/\partial n = 0 \text{ at } S, \quad (4c)$$

$$D: \quad \partial\psi_0/\partial n = 0 \text{ at } S_0, \quad \partial\psi/\partial n = \mu G \text{ at } S, \quad S = S_0, \quad (4d)$$

where μ is small parameter. The functions F and G are known at the surface S_0 . According to (3) we find for:

$$A: \quad N\epsilon = - \int_S \psi_0 \frac{\partial\psi}{\partial n} d\sigma, \quad (5a)$$

$$B: \quad N\epsilon = \mu \int_{S=S_0} F \frac{\partial\psi_0}{\partial n} d\sigma, \quad (5b)$$

⁵This includes $S = S_0$, or the case of the same boundary condition at S and S_0 but $S \neq S_0$.

C:
$$N\epsilon = \int_S \psi \frac{\partial \psi_0}{\partial n} d\sigma, \tag{5c}$$

D:
$$N\epsilon = -\mu \int_{S=S_0} \psi_0 G d\sigma, \tag{5d}$$

with
$$N = \int_S \psi_0 \psi d\tau.$$

§3

First approximation

The above expressions (5a)–(5d) have been obtained without any approximations. We shall now make use of the fact that the change in the boundary condition is small, i.e., that the functions ψ and ψ_0 must be nearly equal. We therefore can put for N

$$N = \int_S \psi_0 \psi d\tau \simeq \int_S \psi_0^2 d\tau \simeq \int_{S_0} \psi_0^2 d\tau = 1.$$

Furthermore, in Eq. (5a) we may replace $\partial\psi/\partial n$ by $\partial\psi_0/\partial n$ and in Eq. (5c) ψ by ψ_0 .^{4, 6} We are now able to calculate ϵ in terms of the known functions ψ_0 , F or G :

A:
$$\epsilon = - \int_S \psi_0 \frac{\partial \psi_0}{\partial n} d\sigma, \tag{6a}$$

B:
$$\epsilon = \mu \int_{S=S_0} \frac{F}{\partial n} d\sigma, \tag{6b}$$

C:
$$\epsilon = \int_S \psi_0 \frac{\partial \psi_0}{\partial n} d\sigma, \tag{6c}$$

D:
$$\epsilon = -\mu \int_{S=S_0} G \psi_0 d\sigma. \tag{6d}$$

Thus, we see that it is possible to determine the first approximation of the energy $E = E_0 + \epsilon$ by an integration over functions which are known from the zero approximation (ψ_0 , $\partial\psi_0/\partial n$) or from the boundary conditions (μF , μG).

⁶ It should be noticed that an analogous proceeding could not be allowed if we had chosen S_0 instead of S as the boundary for the integration in (3). In that case the right-hand side in Eq. (5a), for instance, would be replaced by

$$\int_{S_0} \psi \frac{\partial \psi_0}{\partial n}.$$

Here we cannot insert ψ_0 instead of ψ since $\psi_0 = 0$ at S_0 .

§4

Examples

The expressions for ϵ in the cases A and C may still be simplified considerably if $\psi_0 = \psi_0(r)$ is spherically symmetrical and S_0 is the surface of a sphere with radius r_0 .

Let \mathbf{r}_1 be the radius vector from the origin of the sphere to a point at the surface S_1 . Since S is assumed to be only slightly different from S_0 , we have

$$||\mathbf{r}_1| - r_0| \ll r_0 \tag{7}$$

and
$$|\sin \alpha| \ll 1, \tag{8}$$

where α is the angle between \mathbf{r}_1 and the normal \mathbf{n} to S at the point where \mathbf{r}_1 reaches S . We therefore may develop ψ_0 and $\partial\psi_0/\partial n$, using the fact that ψ_0 is spherically symmetrical:

$$(\psi_0(\mathbf{r}_1))_S = (\psi_0)_{S_0} + (\partial\psi_0/\partial r)_{S_0} \times (|\mathbf{r}_1| - r_0) + \dots, \tag{9}$$

$$\left(\frac{\partial\psi_0(\mathbf{r}_1)}{\partial n}\right)_S = \left(\frac{\partial\psi_0(\mathbf{r}_1)}{\partial r}\right)_S \frac{\partial r_1}{\partial n} = \left\{ \left(\frac{\partial\psi_0}{\partial r}\right)_{S_0} + \left(\frac{\partial^2\psi_0}{\partial r^2}\right)_{S_0} (|\mathbf{r}_1| - r_0) \right\} \cos \alpha + \dots. \tag{10}$$

Case A:—From (6a), we find in the first approximation (i.e., neglecting terms with higher power in $(|\mathbf{r}_1| - r_0)$) using (9), (10), (4a) and (7):

$$\begin{aligned} \epsilon &= - \left(\frac{\partial\psi_0}{\partial r}\right)_{S_0}^2 \int (|\mathbf{r}_1| - r_0) \cos \alpha d\sigma \\ &= - \left(\frac{\partial\psi_0}{\partial r}\right)_{S_0}^2 v. \end{aligned} \tag{11}$$

Here, regarding Eq. (8), v is the difference of the volumes bounded by S and S_0 respectively. v is positive if S includes a greater volume than S_0 .

Case C:—In this case we find from (6c) in the first approximation, using (9), (10), (4c) and (7):

$$\epsilon = (\psi_0 \partial^2\psi_0/\partial r^2)_{S_0} v,$$

where v is the same volume as defined above. Using the Schrödinger equation (1) and Eq. (4c), we find

$$(\partial^2\psi_0/\partial r^2)_{S_0} = [V(r_0) - E_0] \psi_0(r_0)$$

and, therefore, since $(\psi_0)_{S_0} = \psi_0(r_0)$.

$$\epsilon = [V(r_0) - E_0] \psi_0^2(r_0) v. \quad (12)$$

From Eqs. (11) and (12) we see that the first-order perturbation energy is zero if the sphere S_0 is only deformed without a change of volume.

§5

Higher approximations

The higher approximations cannot usually be calculated without solving a partial differential equation.

We do not intend to go into any detail of this question. We just want to mention that it is possible to eliminate the potential from the Schrödinger equation. In order to demonstrate that, we proceed thus: We insert

$$\psi = \psi_0 f$$

into Eq. (2) and observe that ψ_0 obeys Eq. (1). We then obtain for f the differential equation:

$$\text{div}(\psi_0^2 \text{grad } f) + \epsilon \psi_0^2 f = 0.$$

In cases where the function ψ_0 has a simple form, this transformation may be of advantage.³

On the Bose-Einstein Condensation

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A proof is given of the condensation phenomenon of a Bose-Einstein gas. A preliminary discussion of its transport properties is outlined with a view to its possible bearing on the problem of liquid helium.

INTRODUCTION

IN his well-known papers¹ on the degeneracy of an ideal gas, Einstein mentioned a peculiar condensation phenomenon of the ideal "Bose-Einstein" gas. This very interesting discovery, however, has not appeared in the textbooks, probably because Uhlenbeck in his thesis² questioned the correctness of Einstein's argument. Since, from the very first, the mechanism appeared to be devoid of any practical significance, all real gases being condensed at the temperature in question, the matter has never been examined in detail; and it has been generally supposed that there is no such condensation phenomenon.

In discussing some properties of liquid helium, I recently realized that Einstein's statement has been erroneously discredited; moreover, some

support could be given to the idea that the peculiar phase transition ("λ-point"), that liquid helium undergoes at 2.19°K, very probably has to be regarded as the condensation phenomenon of the Bose-Einstein statistics, distorted, of course, by the presence of molecular forces and by the fact that it manifests itself in the liquid and not in the gaseous state. In a preliminary note,³ the course of the specific heat of an ideal Bose-Einstein gas was reproduced, but no proof was communicated. As, since then, I have been asked several times for a proof and as even the correctness of the result has been questioned anew, it might perhaps be justified, on this occasion to publish a quite elementary demonstration of the condensation mechanism, discussing only briefly here the possible connection of the Bose-Einstein degeneracy with the problem of liquid helium.⁴

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¹ A. Einstein, *Ber. Berl. Akad.* 261 (1924); 3 (1925).

² G. E. Uhlenbeck, *Dissertation* (Leiden, 1927).

³ F. London, *Nature* **141**, 643 (1938).

⁴ In a recent paper Uhlenbeck has withdrawn his former objection. G. E. Uhlenbeck and B. Kahn, *Physica* **5**, 399 (1938).