THE METHOD OF PARTIAL WAVES FOR A NONSPHERICAL SCATTERER

Yu. M. DEMKOV and V. S. RUDAKOV

Leningrad State University

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A discussion is given of the S-representation for a nonspherical scatterer which generalizes the usual method of phases for a spherically symmetric problem. It is shown that the behavior of the phases for a low energy of the incident particle is analogous to the spherically symmetric case—they can be classified in terms of the azimuthal quantum number l; there are $2l+1$ phases $\eta_l \sim E^{l+1/2}$. For a symmetric scatterer the partial waves and the phases are classified in terms of the representations of the symmetry group, the degeneracy is determined by the dimension of the representation. A formulation is given of the Hulthen and Schwinger variational principles, of perturbation theory, of the virial theorem, of the Neumann-Wigner theorem concerning the nonintersection of the curves $\eta(E)$ belonging to a single representation of the symmetry group. A discussion is given of the Levinson theorem which connects the behavior of the phases with the number of bound states.

For the case when the scatterer can be represented as a superposition of n potentials of zero range the problem reduces to a purely algebraic one—to the inversion of a matrix of the n-th order. The cross section averaged over the directions of the incident wave is expressed in terms of the trace of the matrix in a form convenient for calculations. Simple examples and cases of resonance are considered. The possibilities are discussed of applying the method, in particular, to the problem of elastic scattering of electrons by molecules.

INTRODUCTION

We consider the scattering of waves or particles in the case when the operator V characterizing the scatterer does not have spherical symmetry. Moreover, we assume that the operator V is self-adjoint, does not depend on the time and falls off sufficiently rapidly as the value of the radius-vector r increases. Then the stationary scattering process is described by the equation

$$(\nabla^2 + k^2 - V)\Psi = 0, \tag{1}$$

where $\mathbf{k}$ is the propagation vector for the incident particle.

The scattering amplitude $f(\nu, n)$ is defined in the usual manner:

$$\Psi \sim e^{ikvr} + f(v, n)\frac{e^{ikr}}{kr}; \quad n = \frac{r}{r}; \tag{2}$$

where ν is the unit vector characterizing the direction of the incident wave.

The effective cross sections—the differential cross section $\sigma(\nu, n)$, the total cross section $\sigma(\nu)$ and the total cross section $\bar{\sigma}$ averaged over all the directions of the incident wave, are defined by the formulas

$$\sigma(v,n) = \frac{1}{k^2}|f(v,n)|, \quad \sigma(v) = \int d n \sigma(v,n), \quad \bar{\sigma} = \frac{1}{4\pi}\int dv\sigma(v), \tag{3}$$

where the integration is carried out over all the directions of the unit vectors n and ν.

The case when the scatterer is not spherically symmetric can be encountered in a wide variety of physical problems described by Eq. (1) such as the scattering of sound or of electromagnetic waves or, for example, the scattering of electrons by a molecule. In the latter case the energy of the electrons should be insufficient for the excitation of the electronic states of the molecule, i.e., it must generally not exceed a value of several eV. But if we assume that the rate of rotation and oscillation of the molecule is considerably smaller than the velocity of the incident electrons, then, knowing the amplitude $f(\nu, n)$, we can easily calculate the probabilities of transitions between the rotational states of the molecule in a collision.

An analogous calculation for the transition between vibrational states can be carried out if we know the scattering for the different configurations $\mathbf{R}$ of atoms in a molecule near the equilibrium position. In this case the operator V depends on $\mathbf{R}$ and we must know the amplitude $f(\nu, n; R)$. Thus, knowing the solution of the problem of elastic scattering, because of the large value of the ratio of the masses of the nuclei and the electrons we can also calculate the inelastic processes associated with the excitation of slow motions in the scatterer.

It should be noted that the problem formulated above (1)–(2) is quite complicated even for the simplest axially symmetric case (of a diatomic molecule) when V is the operator for the potential energy $V(\mathbf{r})$ which is so chosen that the variables are separable in the elliptic system of coordinates (cf., for example, the calculations of the collisions e + H_2[1]).

We consider this problem here by the method of eigenfunctions of the S-matrix which is a natural generalization of the method of partial waves for the scattering by a spherically symmetric scatterer. The S-representation was utilized earlier by a number of authors in different specific problems[2-4]. In connection with the problem concerning the elastic scattering by a nonspherical scatterer this method, as far as we know, has not been investigated previously.

2. THE METHOD OF PARTIAL WAVES

The principal condition for the wave function Ψ to be associated with the eigenfunction of the S-matrix is the requirement that the amplitude of the scattered wave should differ from the amplitude of the incident wave for all the directions n only by a certain factor whose modulus is equal to unity. This condition can be written in the form

$$\Psi_\lambda \sim \frac{1}{2ikr}[A_\lambda(-\mathbf{n})e^{-ikr-i\eta_\lambda} - A_\lambda(\mathbf{n})e^{ikr+i\eta_\lambda}]. \quad (4)$$

The totality of solutions of equation (1) for all possible values of k satisfying condition (4), forms (together with the bound state functions) a complete system of functions. We shall call the functions $A_\lambda(n)$ the characteristic scattering amplitudes, while we shall call $\eta_\lambda(k)$ (which are real for the self-conjugate operator V) the proper phases. It can be easily seen that the shift of the origin of coordinates by a certain vector a does not change the proper phases, while all the amplitudes are multiplied by the phase factor exp(ikna).

We shall prove that the characteristic amplitudes A and A_μ, belonging to different proper phases are orthogonal. For this we utilize the equation

$$\int d\mathbf{r}(\Psi_\mu^*\nabla^2\Psi_\lambda - \Psi_\lambda\nabla^2\Psi_\mu^*) = \int d\mathbf{r}[\Psi_\mu^* V\Psi_\lambda - \Psi_\lambda(V\Psi_\mu)^*]. \quad (5)$$

For the volume of integration we choose a sphere of radius R, we transform the left hand side into a surface integral, we let R approach infinity and we utilize formula (4) for the asymptotic form of the functions Ψ_λ, and Ψ_μ. The right hand side of the equation will tend to zero as a result of the self-adjoint nature of V, and we obtain

$$\frac{1}{k}\sin(\eta_\lambda - \eta_\mu)\int d\mathbf{n}A_\mu^*(\mathbf{n})A_\lambda(\mathbf{n}) = 0. \quad (6)$$

We note that the proper phases are determined by equation (4) up to an additive term which is a multiple of π, and, thus, the condition of orthogonality has been demonstrated. If degeneracy is present and several partial waves Ψ_λ and characteristic amplitudes A_λ correspond to a single value of η_λ, then they are determined up to a linear transformation among them, and we can carry out orthogonalization by the usual methods as a result of which we obtain orthogonal amplitudes defined up to a unitary transformation in the subspace of a given proper phase.

We can choose the normalizing factor for the functions Ψ_λ in such a manner that the characteristic amplitudes A_λ would satisfy the normalization condition. After this the totality of the functions $A_\lambda(n)$ for each value of k forms a complete system of orthonormal functions on the surface of a unit sphere.

In the simplest case when the scatterer is spherically-symmetric, the partial waves Ψ_λ are given by the wave functions

$$\Psi_{lm} \doteq \frac{1}{kr}u_l(r)Y_{lm}(\mathbf{n}), \quad (7)$$

the characteristic amplitudes A_λ are given by the spherical harmonics Y_{lm}, while the proper phases are given by the usual phases η_l determined by the asymptotic form of the radial equation

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} - V(r)\right]u_l = 0, \quad u_l \sim \sin\left[kr - \frac{l\pi}{2} + \eta_l\right]. \quad (8)$$

In this case we have degeneracy corresponding to the spherical symmetry of the problem—the phases depend only on the angular momentum (l), but not on its component (m).

In the general case, if the scatterer possesses some additional symmetry group (the most obvious ones are the different types of point groups—axial, cubic etc. symmetries), all the partial waves can be classified in terms of the representations of these groups; the degeneracy will be determined by the existence of representations of dimension greater than unity, i.e., it will always occur in the case of a noncommutative symmetry group.

We now express the usual scattering amplitude $f(\nu, n)$ in terms of the characteristic amplitudes $A_\lambda(n)$ and the proper phases $\eta_\lambda(k)$. For this we write the asymptotic formula (2) in the form

$$\Psi \sim \frac{4\pi}{2ikr}\left[\delta(\mathbf{v}+\mathbf{n})e^{-ikr} - \left(\delta(\mathbf{v}-\mathbf{n}) - \frac{2i}{4\pi}f(\mathbf{v},\mathbf{n})\right)e^{ikr}\right]. \quad (9)$$

The expansion of the function Ψ in terms of the partial waves Ψ_λ is determined by the form of the coefficient in front of the convergent wave. We have

$$\delta(\mathbf{v}+\mathbf{n}) = \sum_\lambda A_\lambda^*(\mathbf{v})A_\lambda(-\mathbf{n}), \quad (10)$$

whence we obtain

$$\Psi = 4\pi\sum_\lambda e^{i\eta_\lambda}A_\lambda^*(\mathbf{v})\Psi_\lambda, \quad (11)$$

$$f(\mathbf{v},\mathbf{n}) = \frac{4\pi}{2i}\sum_\lambda (e^{2i\eta_\lambda} - 1)A_\lambda^*(\mathbf{v})A_\lambda(\mathbf{n}). \quad (12)$$

Finally, for the total and for the averaged effective cross sections we obtain

$$\sigma(\mathbf{v}) = \frac{(4\pi)^2}{k^2}\sum_\lambda |A_\lambda(\mathbf{v})|^2\sin^2\eta_\lambda, \quad \bar{\sigma} = \frac{4\pi}{k^2}\sum_\lambda \sin^2\eta_\lambda. \quad (13)$$

All these formulas go over into the usual formulas of the method of phases for a spherically symmetric case.

3. BEHAVIOR OF THE PHASES AT LOW ENERGIES

The index λ by means of which we number the proper phases for the spherically symmetric case can be replaced by two indices: l and m which have a simple physical meaning. The question arises, how should we classify the partial waves in the general case? One of the possible methods is the consideration of their behavior at low energies, i.e., for $k \to 0$. In this case the wavelength of the particle will be large compared to the dimensions of the scatterer and the results must in some sense approach the results of the spherically symmetric problem. In particular, we shall see that the proper phases can be classified by the azimuthal quantum number l, so that for $k \to 0$ the phase $\eta_\lambda \sim k^{2l+1}$, while the corresponding characteristic amplitude tends to some spherical harmonic $Y_l(n)$.

In order to obtain this result we shall investigate to what limit does the partial wave Ψ_λ tend as $k \to 0$ if the phase is $\eta_\lambda \sim k^{2l+1}$. For large r where the operator V can be neglected the solution will be a general solution of the Laplace equation:

$$\Psi \sim \sum_{l=0}^{\infty}\sum_{m=-l}^{l}(c_{lm}r^l + d_{lm}r^{-l-1})Y_{lm}(\mathbf{n}). \quad (14)$$

For small but nonzero values of k this same solution

can be written outside the scatterer in the form of a general solution of the Helmholz equation $(\nabla^2 + k^2)\Psi = 0$:

$$\Psi \sim \sum_{l=0}^{\infty} \sum_{m=-l}^{l} [C_{lm} R_l^r(kr) + D_{lm} R_l^i(kr)] Y_{lm}(\mathbf{n}), \tag{15}$$

where R_l^r and R_l^i are the regular and the irregular radial functions of the solutions of the Helmholz equation

$$R_l^r = \sqrt{\frac{\pi}{2kr}} J_{l+1/2}(kr), \quad R_l^i = \sqrt{\frac{\pi}{2kr}} J_{-l-1/2}(kr), \tag{16}$$

which behave for small values of r like

$$R_l^r \sim \frac{(kr)^l}{(2l+1)!!}, \quad R_l^i \sim \frac{(kr)^{-l-1}}{(2l-1)!!}, \tag{17}$$

while for large values of r have the form

$$R_l^r \sim \sin\left(kr - \frac{l\pi}{2}\right), \quad R_l^i \sim \cos\left(kr - \frac{l\pi}{2}\right). \tag{18}$$

In order for A_λ to be a characteristic function of the S-matrix it is necessary and sufficient in accordance with (4) (taking into account the parity $(-1)^l$ of the spherical harmonics) that the ratio

$$D_{lm}/C_{lm} = \operatorname{tg}\eta \tag{19}$$

should not depend on l and m. From a comparison of formulas (14), (15), (17), and (18) it can be seen that if $\operatorname{tg}\eta \sim k^{2l_0+1}$, then in the limit $k \to 0$ we can obtain nonzero values of the coefficients c_l, d_l only for $l = l_0$. Also in this case $C_{l_0 m} \sim k^{-l}$ and $D_{l_0 m} \sim k^{l+1}$. For all the other spherical harmonics $c_{lm} = 0$ for $l > l_0$, and $d_{lm} = 0$ for $l < l_0$. Thus, in the limit $k \to 0$ the wave function Ψ_λ must have the form

$$\Psi_{l_0} \sim \sum_{l=0}^{l_0} \sum_{m=-l}^{l} c_{lm} r^l Y_{lm}(\mathbf{n}) + \sum_{l=l_0}^{\infty} \sum_{m=-l}^{l} d_{lm} r^{-l-1} Y_{lm}(\mathbf{n}). \tag{20}$$

For $l = l_0$ the ratio $\gamma = d_{l_0 m}/c_{l_0 m}$ must not depend on m. Then we have

$$\operatorname{tg}\eta \sim \gamma k^{2l_0+1} + O(k^{2l_0+3}). \tag{21}$$

In other words, if the phase is proportional to k^{2l_0+1}, then for the harmonics with $l < l_0$ as $k \to 0$ it tends to zero too rapidly, so that in the limit only the regular solution is left. But if $l > l_0$, then for $k \to 0$ the phase will vanish too slowly and in the limit only the irregular solution remains. And only for $l = l_0$ will both solutions be preserved in the limit.

The inverse assertion is also valid: if there exists a solution of the equation

$$\nabla^2\Psi = V\Psi, \tag{22}$$

which has the asymptotic form (20), then there exists a partial wave with the proper phase $\eta \sim k^{2l_0+1}$, which in the limit $k \to 0$ goes over into this solution.

We shall show that such solutions indeed exist, and for each value of l there exist, in the general case, $2l + 1$ such solutions. In order to show this we consider the solutions of equation (22) satisfying the integral equation

$$\Phi_{lm} = r^l Y_{lm}(\mathbf{n}) - \frac{1}{4\pi} \int d\mathbf{r}' \frac{V(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \Phi_{lm}(\mathbf{r}'). \tag{23}$$

If the operator V falls off sufficiently rapidly, then the iteration process converges and the unique solution of this equation can be easily constructed. It is evident that the solution has the asymptotic form

$$\Phi_{l_0 m_0} \sim r^l Y_{l_0 m_0}(\mathbf{n}) + \sum_{l=0}^{\infty} \sum_{m=-l}^{l} g_{lm}^{l_0 m_0} r^{-l-1} Y_{lm}(\mathbf{n}). \tag{24}$$

We can now sequentially construct from these functions the functions $\varphi_{l_0 m_0}$ which have the asymptotic form (20). It is evident that Φ_{00} itself satisfies the condition (20) for $l_0 = 0$. Further we must exclude from the summation over l in (24) the lowest terms. We obtain

$$\varphi_{00} = \Phi_{00}, \quad \varphi_{1m} = \Phi_{1m} - \frac{g_{00}^{1m}}{g_{00}^{00}} \Phi_{00}, \ldots. \tag{25}$$

Here in order to eliminate the l_0^2 lowest terms in the expansion (24) each time we have l_0^2 functions Φ_{lm} with $l < l_0$. Thus, we obtain the set of functions φ_{lm} with the asymptotic form

$$\varphi_{l_0 m_0} \sim \sum_{l=0}^{l_0-1} \sum_{m=-l}^{l} p_{lm}^{l_0 m_0} r^l Y_{lm}(\mathbf{n}) + r^{l_0} Y_{l_0 m_0}(\mathbf{n}) + \sum_{l=l_0}^{\infty} \sum_{m=-l}^{l} q_{lm}^{l_0 m_0} r^{-l-1} Y_{lm}(\mathbf{n}). \tag{26}$$

However, these functions do not yet satisfy all the requirements since the coefficients for the regular and the irregular solutions are not proportional for $l = l_0$. If we now construct the linear combination

$$\Psi_{l_0} = \sum_{m=-l_0}^{l_0} h_{l_0 m}^{l_0 \mu} \varphi_{l_0 m} \tag{27}$$

and require such proportionality, then we will have constructed the desired functions. In this case the problem reduces to the diagonalization of a matrix of order $2l_0 + 1$ of the coefficients $q_{l_0 m}^{l_0 m_0}$.

It is not difficult to prove that this matrix is Hermitean. The $2l + 1$ eigenvalues of this matrix $\gamma_{l_0 \mu}$ ($\mu = -l_0, -l_0 + 1, \ldots, l_0$) determine the $2l_0 + 1$ phases $\eta_{l_0 \mu} \sim k^{2l_0+1}$ and $2l_0 + 1$ characteristic scattering amplitudes which in the limit $k \to 0$ will tend to the given linear combinations of spherical harmonics:

$$A_{l_0 \mu} = \sum_{m=-l_0}^{l_0} h_{l_0 m}^{l_0 \mu} Y_{l_0 m}(\mathbf{n}) \tag{28}$$

—combinations which are determined by the explicit form of the potential V. (Of course, one can not in the general case assign to the index μ some simple meaning, such as, for example, the component of the angular momentum.)

Thus, the assertion formulated above concerning the classification of the phases has been proved. This classification enables one to make an estimate as to what number of phases make an appreciable contribution to the cross section in slow collisions. If the effective radius of the scatterer is R, then, evidently, the quantity $L = kR$ determines the maximum angular momentum which makes an appreciable contribution to the cross section. Then the phases η_l with $l < L$ will differ appreciably from zero, while for $l > L$ the phases will be small and their contribution to the scattering will fall off rapidly with increasing l. If $kR_0 \ll 1$, then the scattering with $l = 0$ will predominate and the problem reduces to finding the solution of equation (22) with the asymptotic form:

$$\Psi_0 \sim 1 - \frac{a}{r} + O\left(\frac{1}{r^2}\right) \tag{29}$$

or of the equivalent integral equation

$$\Psi_0 = 1 - \frac{1}{4\pi}\int dr' \frac{V(r')}{|r-r'|}\Psi_0. \tag{30}$$

The scattering length

$$a = \frac{1}{4\pi}\int dr V(r)\Psi_0(r) \tag{31}$$

determines the limit to which the effective cross section tends

$$\sigma_{k\to 0} = 4\pi a^2, \tag{32}$$

and in the limit the scattering becomes isotropic.

We do not consider here special cases when one of the coefficients γ_l vanishes. Then the corresponding phase will be proportional to k^{2l+3} or to higher powers of k. The resonance case is also a special case when the corresponding bound state reaches the limit of the continuous spectrum. In this case the integral equation (23) does not have a solution since there exists a solution of the corresponding homogeneous equation. Then tg η_l tends to zero slower than k^{2l+1}.

4. THE VARIATIONAL PRINCIPLE

We formulate the variational principles which enable one to determine the partial waves and the proper phases by direct methods. For the sake of simplicity we restrict ourselves to the case when the operator V has the form of a local potential energy operator V(r). We seek the solution of equation (1) with the boundary condition (4) in the form

$$\Psi_\lambda = \int dr' \chi_\lambda(r') \frac{\sin(k|r-r'|+\eta_\lambda)}{k|r-r'|}. \tag{33}$$

Investigating the asymptotic behavior of the right hand side of this equation under the assumption that V(r) falls off sufficiently rapidly with increasing r it is easy to show that condition (4) is satisfied automatically for any χ, while the scattering amplitude has the form

$$A_\lambda(n) = -\int dr' e^{ikn r'} \chi_\lambda(r'). \tag{34}$$

Substituting (32) into (1) we obtain the equation which must be satisfied by the function χ:

$$\frac{4\pi}{V(r)}\chi_\lambda(r) + \int dr' \frac{\cos(k|r-r'|)}{|r-r'|}\chi_\lambda(r') = -\operatorname{ctg}\eta_\lambda \int dr' \frac{\sin(k|r-r'|)}{|r-r'|}\chi_\lambda(r'). \tag{35}$$

Using this integral equation and regarding $-\cot\eta_l$ as eigenvalues we arrive at a functional the stationary values of which will be the quantities:

$$-[\operatorname{ctg}\eta_\lambda] = \frac{\mathcal{A}}{\mathcal{B}};$$

$$\mathcal{A} = 4\pi\int dr \frac{|\chi_\lambda(r)|^2}{V(r)} + \iint dr\, dr' \chi_\lambda^*(r)\frac{\cos(k|r-r'|)}{|r-r'|}\chi_\lambda(r'),$$

$$\mathcal{B} = \iint dr\, dr' \chi_\lambda^*(r)\frac{\sin(k|r-r'|)}{|r-r'|}\chi_\lambda(r'). \tag{36}$$

The function χ_λ which in accordance with formula (33) can be called the distribution function for the sources for the partial wave must evidently vanish everywhere where V(r) vanishes, while for decreasing V(r) it must vanish sufficiently rapidly so that the first integral in the numerator of formula (36) would converge.

The denominator of this formula $\mathcal{B}$ can be represented by utilizing (34) in the form

$$\iiint dr\, dr'\, dn\, \chi_\lambda^*(r) e^{ikn|r-r'|}\chi_\lambda(r') = \int dn |A_\lambda(n)|^2, \tag{37}$$

from which it can be seen that the denominator is a nonnegative quantity. If the denominator were positive definite then the given variational principle would have allowed us in variational calculations to approach the exact values of the phases from one side, since the set of values of $-\cot\eta_\lambda$ is bounded from above or from below respectively for a negative or a positive V(r). However, in actual fact it is easy to construct such functions $\chi(r)$ for the distribution of sources which quench all the scattered waves and the amplitude A(n) vanishes for all values of n. For this it is sufficient (and necessary) that the Fourier transform of the function $\chi(r)$ would vanish on the surface of a sphere of radius k in momentum space. Thus, the operator with the kernel $\sin(k|r-r'|)/|r-r'|$ is similar to a projection operator and accordingly in the general case we do not obtain a definite variational principle. However, in some special cases, as we shall see below, the positive definiteness of the denominator $\mathcal{B}$ and, correspondingly, the definiteness of the variational principle (36) can be guaranteed.

In the spherically symmetric case the variational principle (36) goes over into the well known variational principle of Schwinger[5]. It is interesting that the potential V(r) which characterizes the scatterer appears only in the single integral in the numerator, and this, in principle, facilitates direct calculations for different potentials V in accordance with this method.

We now formulate a variational principle, analogous to the variational principle of Hulthen for the spherically symmetric case. In order to do this we consider the functional

$$J(\Phi_1, \Phi_2) = \int dr\, \Phi_2^*(\nabla^2 + k^2 - V)\Phi_1, \tag{38}$$

in which the asymptotic form of the functions Φ_1 and Φ_2 is determined by formula (4) with the normalized amplitudes $A_1(n)$ and $A_2(n)$ and the phases η_1 and η_2 respectively, and these amplitudes and phases need not coincide with the corresponding quantities for the exact partial waves.

We represent the functions Φ_1 and Φ_2 in the form $\Phi_1 = \Psi_\lambda + \Delta\Phi_1$ and $\Phi_2 = \Psi_\lambda + \Delta\Phi_2$, where Ψ_λ is the exact partial wave with the amplitude $A_\lambda(n)$ and the phase η_λ, and we substitute these expressions into the functional (38). After standard transformations we obtain

$$J = \frac{1}{k}\sin(\eta_\lambda - \eta_1)\int dn\, A_\lambda^*(n)A_1(n) + \int dr \Delta\Phi_2^*(\nabla^2 + k^2 - V)\Delta\Phi_1. \tag{39}$$

If we now assume that $\Delta\Phi_1$ and $\Delta\Phi_2$ are small and set $\eta_1 - \eta_\lambda = \delta_1\eta$, we then arrive at Hulthen's variational principle

$$\delta J = -k^{-1}\delta_1\eta, \tag{40}$$

and the phase can be obtained as the stationary value of the functional

$$[\eta] = \eta_1 + kJ(\Phi_1, \Phi_2). \tag{41}$$

From the variational principle thus obtained it is

easy to obtain all those consequences which are obtained from Hulthen's variational principle for the spherically symmetric case. For example, by varying the scale we obtain the formulation of the virial theorem[6],

$$\frac{d\eta_\lambda}{dk} = \int d\mathbf{r}\, \Psi_\lambda^* (2V + \mathbf{r}\nabla V)\Psi_\lambda. \quad (42)$$

If to the potential V we add the small perturbation V_1, then from the variational principle (41) the formula immediately follows for the correction to the phase η_λ in the first approximation of perturbation theory:

$$\Delta^{(1)}\eta_\lambda = -k \int d\mathbf{r}\, \Psi_\lambda^* V_1 \Psi_\lambda. \quad (43)$$

But this formula is valid only in the absence of degeneracy. But if in the unperturbed problem degeneracy is present, then it is necessary to diagonalize the matrix V_1 in the subspace of the degenerate functions Ψ_λ in exactly the same way as in the stationary perturbation theory for energy levels.

From this result the Neumann-Wigner theorem for the phases follows immediately: if when k is varied two phases η_1 and η_2 coincide, then this requires that another subsidiary condition be satisfied, and a small perturbation of a sufficiently general form will lead to the fact that the crossing will be replaced by a pseudo-crossing. The crossing is possible and the subsidiary conditions are satisfied automatically if the partial waves and phases belong to different representations of the symmetry group of the scatterer, for example the phases η_l for a spherically symmetric problem.

5. SCATTERING BY A SYSTEM OF POTENTIALS OF ZERO RANGE

We consider the case when the scatterer can be regarded as a set of potentials of zero range situated at the points $\mathbf{r}_j$ (j = 1, 2, ... n). Then at these points the wave function must satisfy the boundary conditions

$$\Psi_{\mathbf{r}\to\mathbf{r}_j} = s_j\left(\frac{1}{|\mathbf{r}-\mathbf{r}_j|} - \alpha_j\right) + O(|\mathbf{r}-\mathbf{r}_j|), \quad (44)$$

where α_j are parameters characterizing the depth of each potential well. If $\alpha > 0$, then in an isolated well there exists a bound state with the energy $-\alpha^2/2$, $(\psi \sim e^{-\alpha r}/r)$; if $\alpha < 0$, then there is no bound state. As $\alpha_j \to -\infty$ the well disappears, $s_j \to 0$ and ψ in the limit has no singularity at the point $\mathbf{r}_j$. Outside the points $\mathbf{r}_j$ the wave function must evidently in our case satisfy the equation for a free particle.

We seek the solution of the scattering problem (positive energy) for the partial wave Ψ in the form

$$\Psi = \sum_{j=1}^{n} c_j \frac{\sin(k|\mathbf{r}-\mathbf{r}_j| + \eta)}{|\mathbf{r}-\mathbf{r}_j|}. \quad (45)$$

We require that for this function the boundary conditions (44) should be satisfied. We obtain the system of homogeneous equations:

$$\sum_{j\neq i}^{n} c_j \frac{\sin(k|\mathbf{r}_i-\mathbf{r}_j| + \eta)}{|\mathbf{r}_i-\mathbf{r}_j|} + c_i(k\cos\eta + \alpha_i \sin\eta) = 0, \quad i = 1, 2, \ldots, n. \quad (46)$$

If we denote

$$M_{ij} = \frac{\cos kr_{ij}}{r_{ij}}, \quad N_{ij} = \frac{\sin kr_{ij}}{r_{ij}} \quad (i \neq j); \quad M_{ii} = \alpha_i, \quad N_{ii} = k, \quad (47)$$

then the proper phases can be obtained from the secular equation

$$\det|M_{ij} + \operatorname{ctg}\eta N_{ij}| = 0. \quad (48)$$

Thus, we have only n proper phases which differ from zero (this assertion is valid for any separable potential $V = \sum_{j=1}^{n} |\varphi_j\rangle\langle\varphi_j|$).

The matrix N is positive[1]. From this it follows that $\sin\eta_l$ can not vanish for $k \neq 0$. Consequently each phase η_λ can vary only in the interval $0 < \eta_l < \pi$ (in contrast, for example, to the spherically symmetric case, which can not be realized by a choice of a finite number of potentials of zero range). This assertion is closely related to Levinson's theorem[7] according to which the total value of all the phases for k = 0 is equal to $s\pi$, where s is the number of bound states of the system. Thus, we obtain in our case a pairwise correspondence between n partial phases and n possible bound states. If a bound state actually exists, then the corresponding phase at zero is equal to π, but if it is absent, i.e., if for given parameters of the problem (α_j, r_{ij}) the pole of the Green's function is situated on a nonphysical sheet of the complex energy surface, then the corresponding phase at zero is equal to zero.

We now transform the linear problem (46)–(48) in such a manner as to obtain a compact expression for the averaged total effective cross section $\bar{\sigma}$. We have

$$MC = -NC\operatorname{ctg}\eta, \quad N^{-1/2}MN^{-1/2}C' = LC' = -C'\operatorname{ctg}\eta, \quad (49)$$

$$(1+L^2)^{-1}C' = C'\sin^2\eta, \quad N^{1/2}(M+iN)^{-1}N(M-iN)^{-1}N^{1/2}C' = C'\sin^2\eta;$$

$$\bar{\sigma} = \frac{4\pi}{k^2}\operatorname{Sp}[N(M+iN)^{-1}N(M-iN)^{-1}]. \quad (50)$$

Formula (50) is a generalization of the simple resonance formula

$$\sigma = 4\pi/(k^2+\alpha^2) \quad (N = k, M = \alpha) \quad (51)$$

for a single well of zero range.

Thus, the problem reduces to the inversion of one complex symmetric matrix P of order n:

$$P = M + iN, \quad P_{ij} = \frac{e^{ikr_{ij}}}{r_{ij}} \quad (i \neq j), \quad P_{ii} = \alpha_i + ik, \quad (52)$$

to the multiplication of the matrixes N, P^{-1}, N, and $(P^{-1})^*$ and to the evaluation of a trace.

If k is large, so that all the $kr_{ij} \gg 1$ and $k\alpha_j \gg 1$, then all the phases are close to $\pi/2$ so that $\cot\eta \sim k^{-1}$. Then in formula (50) we can set $N \sim kI$ and $N \gg M$ and obtain the first two terms of the expansion in inverse powers

$$\bar{\sigma} = \frac{4\pi}{k^2}\left(N - \frac{1}{k^2}\operatorname{Sp}M^2 + \ldots\right) = \frac{4\pi}{k^2}\left[\sum_i (k^2+\alpha_i^2)^{-1} + \frac{L(k)}{k^2} + \ldots\right], \quad (53)$$

where L(k) is the oscillating part of the quantity $\operatorname{Sp} M^2$.

Thus, in the limit, after averaging over a certain

[1] The quadratic form $\Sigma N_{ij}C_iC_j$ is analogous to the denominator $\mathcal{D}$ in formula (36). It is sufficiently obvious that by varying the intensities of the sources c_i at the points $\mathbf{r}_i$, we can not guarantee the elimination (due to interference) of the scattered wave in all directions $\mathbf{n}$, and, thus, the positive definiteness in this particular case does indeed hold.

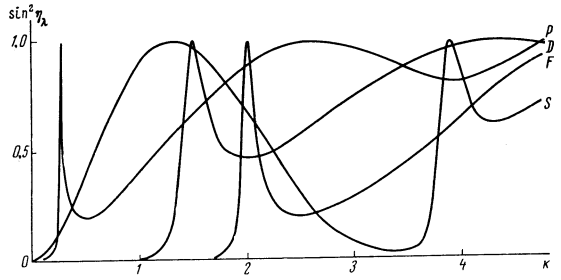

FIG. 1. The dependence of $\sin^2\eta_\lambda$ on k for the S, P, D and F partial waves; $\alpha = 0.2$. All the phases oscillate near $\pi/2$. For the S-phase for k = 3.5 one can see the effect of "replusion by zero".

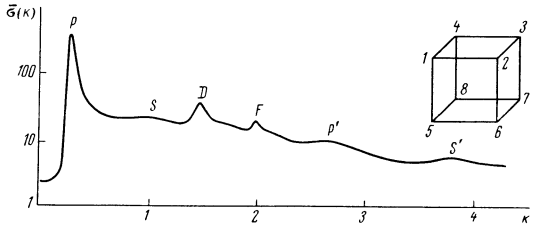

FIG. 2. The dependence on k of the total averaged scattering cross section. On the right hand side is given the method of numbering the scatterers. It is noted, as to which partial waves do the resonance maxima belong.

interval $\Delta k \sim r_{ij}^{-1}$ we obtain an apparently independent scattering by all the n centers. However, in this case just those properties of our model potentials are manifested which make it differ from the smooth potentials V(r), in particular, the tendency of all the phases to approach $\pi/2$.

If we consider the scattering of an electron by a molecule, then the simplest and most natural approximation will be the replacement of each atom in the molecule by a potential of zero range. In such a case the energy of the electron must not be too low, since the approximation does not take into account polarization forces, and must not be too large, since we are not taking into account the electronic excitation of the molecule (a typical range is from several tenth's of eV to several eV). In carrying out systematic calculations one can doubtless propose recipes for determining α_j (the simplest choice is $\alpha_j = a_j^{-1}$, where a_j is the scattering length for the corresponding isolated atom) taking into account the nature of the binding, its length, its surrounding etc.

The approximation of zero range potentials is widely utilized for the scattering of neutrons by nuclei in molecules or in crystals (cf., also[8,9]). But in this case the scattering amplitude is simply a superposition of the amplitudes for the scattering by each nucleus. In this case the scattering cross section is considerably smaller than the dimensions of the molecule and one can neglect multiple scattering. In our case such an approximation is not allowable, and within the framework of the given model multiple scattering is taken into account exactly.

6. EXAMPLE

In those cases when the scatterer—a system of potentials of zero range—possesses high symmetry, the coefficients c_j of the solution of the system (46) can be obtained immediately from the symmetry properties. Thus, for example, for two identical wells of short range we have the solutions S(+1, +1) and P(+1, −1). For eight identical wells, situated at the vertices of a cube, we have one monopole solution S of the type (+1, +1, +1, +1, +1, +1, +1, +1), three dipole solutions P of the type (+1, +1, +1, +1, −1, −1, −1, −1) three quadrupole solutions D of the type (+1, +1, −1, −1, −1, −1, +1, +1), and one octopole solution F of the type (+1, −1, +1, −1, +1, −1, +1, −1). (The numbering of the vertices of the cube is given below in Fig. 2). Denoting the distance between nearest wells by R and measuring the cross section in units of R^2, and k and α in units of R^{-1}, we obtain without any intermediate calculations the averaged cross section for two wells (cf.,[10]):

$$\bar{\sigma} = \frac{4\pi}{k^2}\left\{\left[1+\left(\frac{\alpha+\cos k}{k+\sin k}\right)^2\right]^{-1} + \left[1+\left(\frac{\alpha-\cos k}{k-\sin k}\right)^2\right]^{-1}\right\} \quad (54)$$

and for a cubic configuration

$$\bar{\sigma} = \frac{4\pi}{k^2}\cdot$$

$$\cdot\left\{\left[1+\left(\frac{\alpha+3\cos k+(3/\sqrt{2})\cos k\sqrt{2}+(1/\sqrt{3})\cos k\sqrt{3}}{k+3\sin k+(3/\sqrt{2})\sin k\sqrt{2}+(1/\sqrt{3})\sin k\sqrt{3}}\right)^2\right]^{-1} \text{(monopole)}\right.$$

$$+3\left[1+\left(\frac{\alpha+\cos k-(1/\sqrt{2})\cos k\sqrt{2}-(1/\sqrt{3})\cos k\sqrt{3}}{k+\sin k-(1/\sqrt{2})\sin k\sqrt{2}-(1/\sqrt{3})\sin k\sqrt{3}}\right)^2\right]^{-1} \text{(dipole)}$$

$$+3\left[1+\frac{\alpha-\cos k-(1/\sqrt{2})\cos k\sqrt{2}+(1/\sqrt{3})\cos k\sqrt{3}}{k-\sin k-(1/\sqrt{2})\sin k\sqrt{2}+(1/\sqrt{3})\sin k\sqrt{3}}^2\right]^{-1} \text{(quadrupole)}$$

$$\left.+\left[1+\left(\frac{\alpha-3\cos k+(3/\sqrt{2})\cos k\sqrt{2}-(1/\sqrt{3})\cos k\sqrt{3}}{k-3\sin k+(3/\sqrt{2})\sin k\sqrt{2}-(1/\sqrt{3})\sin k\sqrt{3}}\right)^2\right]^{-1}\right\} \text{ octopole)} \quad (55)$$

where the square brackets indicate the contributions of the corresponding partial waves. Resonance peaks arise if the numerator within the curved brackets vanishes for a certain k, while the value of the denominator for the same value of k is small. Then the corresponding phase is equal to $\pi/2$ and the contribution of the given partial wave is at a maximum. Particularly narrow resonances are obtained for higher multipoles for small k, since for $k \to 0$ the denominators are proportional to k^{2l+1}, so that if the resonance is situated at $k \sim k_0$, then the width of the maximum is given by $\Delta k \sim k_0^{2l+1}$, just as for the spherically symmetric case[11].

The presence of trigonometric functions in the formulas leads to an oscillation in the cross section associated with diffraction effects, when the wave length is by an integral number of times smaller than the distance between the wells. Figure 2 gives the results of calculations by formula (55) for the value $\alpha = 0.2$. In Fig. 1 the contributions of the different partial waves are singled out.

7. CONCLUSION

We thus see that the method of partial waves for a nonspherical scatterer has many properties which are analogous to the spherically symmetric case. Its main advantage consists of the fact that the asymmetry associated with the existence of a plane incident wave

is here taken into account at the very last stage (and in the evaluation of $\bar{\sigma}$ this asymmetry does not appear at all). This enables us, in particular, to take into account in the most natural manner the symmetry of the scatterer.

Of course, the calculation of partial waves for a specific potential $V(r)$ is a sufficiently complicated problem, but this complexity is an internal feature of the problem itself, and is not a defect of the method. The calculation of partial waves resembles the calculation of energy levels for bound states, so that in utilizing it a certain kind of symmetry appears in considering bound states (negative energy) and scattering (positive energy). The existence of variational principles which enable one to calculate the phases and the partial waves by direct methods also demonstrates this symmetry.

In analogy with the spherically symmetric case, there is every reason to assume that in slow collisions (the wave length is greater than or comparable to the dimensions of the scatterer) the method of partial waves is the most convenient one for the investigation and the calculation of scattering by nonspherical systems.

In conclusion we thank G. F. Drukarev and L. D. Faddeev for discussing this work and for valuable comments.

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