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Note

On the Evaluation of the Principal Value Integral in the Scattering Problems*

The purpose of this note is to discuss the evaluation by a differential equation method of a class of principal value integrals that occur frequently in atomic and molecular physics. In the quantum mechanical perturbation calculations for scattering processes, one often deals with the matrix expression of the form [1, 2]

$$J = \lim_{\eta \to 0} \langle \phi_f \mid H'' \frac{1}{E_0 - H_0 + i\eta} H' \mid \phi_i \rangle, \tag{1}$$

where H_0 is Hermitian and $E_0 = k_0^2$ is positive. As is well known [3], the meaning of the expression $(1/E_0 - H_0 + i\eta)$ in Eq. (1) denotes that the value J contains two parts: a principal value integral part P and an imaginary part I,

$$\frac{1}{E_0 - H_0 + i\eta} = \frac{P}{E_0 - H_0} - i\pi\delta(E - H_0). \tag{2}$$

The principal value integral part P can be better expressed, on inserting a complete set of eigenstates φ_k of H_0 between H'' and H', in the matrix form as

$$P = P\left(\int_k \Sigma'\right) \frac{\langle \phi_f \mid H'' \mid \varphi_k \rangle \langle \varphi_k \mid H' \mid \phi_i \rangle}{k_0^2 - E_k}, \tag{3}$$

where the principal value summation $\int_k \Sigma'$ contains both bound and continuum intermediate state φ_k.[1]

In general, a straightforward evaluation of the principal value integral P by numerical integration of the matrix elements is rather difficult. The difficulty lies in the fact that the integrands in Eq. (3) become increasingly large as k approaches the singularity k_0 from above and below. The principal value P must be obtained as the difference between two large, near-equal numbers, rendering the numerical result rather unreliable. Moreover, for atomic and molecular applications, the analytic behavior of the matrix elements in the integrand is, in general, not known, so that mathematical "tricks" (for instance, Taylor expansions from k_0) cannot always be used near the singularity region.

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[1] In general, the determination of the asymptotic boundary conditions for ϕ_i, ϕ_f, and φ_k depends on each individual physical process. Usually they are to be well behaved at the origin and bounded ($E_0 < 0$) or oscillatory ($E_0 > 0$) at infinity. There are many discussions on this subject in the literature. See, for instance, A. BURGESS, *Proc. Phys. Soc.* **81** (1963), 442.

We suggest that this class of principal value integrals can be effectively and accurately evaluated by the differential equation approach as outlined below.

In the differential equation approach, we define a function Φ,

$$\Phi = \frac{P}{E_0 - H_0} H' \mid \phi_i\rangle = P \int_k \Sigma' \frac{\mid \varphi_k\rangle\langle\varphi_k \mid H' \mid \phi_i\rangle}{E_0 - E_k}. \tag{4}$$

The function Φ is equivalent to the solution of the differential equation

$$(k_0^2 - H_0)\,\Phi = H'\phi_i\,, \tag{5}$$

with appropriate boundary conditions. The first boundary condition is relatively trivial. We recognize, on examining Eq. (4), that Φ must be well behaved at the origin. The second boundary condition is less transparent, and, in fact, forms the main motivation for this communication. We recognize that, since H_0 is Hermitian, and therefore φ_k's are orthonormal, Φ must be orthogonal to φ_{k_0}. As both Φ and φ_{k_0} are in the continuum, and in fact, have the same wave numer, the orthogonality condition between Φ and φ_{k_0}—translated into a simpler language—says that they must differ by $\pi/2$ in phase, asymptotically. That is, in obtaining the desired

$$\Phi = \phi^p + A\phi^h \tag{6}$$

from Eq. (5), the combination of the particular solution with the homogeneous solution ϕ^h ($\equiv \varphi_{k_0}$), i.e., the determination of coefficient A, must be such that the phase of Φ is $\pi/2$ away from that of φ_{k_0}.

With Φ thus obtained, the principal value integral we sought is, simply,

$$P = \langle\phi_f \mid H'' \mid \Phi\rangle. \tag{7}$$

The present approach has been extensively tested and employed in a number of calculations, such as the double electron ejection process by photosorption [4]. These applications have shown that this method is particularly effective in yielding fast and accurate results.

We conclude with some relevant comments on the method. For bound-state type perturbation calculations, the differential equation type of approach, as outlined above, has been quite extensively utilized [5, 6]. However, for the bound-state conditions, the troublesome singularity does not occur, and the straightforward matrix-element integration can be effectively carried out. Furthermore, for bound-state conditions, one may neglect the second boundary condition (the orthogonality condition) in solving for Φ, and still obtain the desired P by projecting out φ_{k_0} components afterwards,

$$P = \langle\phi_f \mid H'' \mid \Phi\rangle - \langle\phi_f \mid H'' \mid \varphi_{k_0}\rangle\langle\varphi_{k_0} \mid \Phi\rangle. \tag{8}$$

In contrast, it is absolutely necessary for the present scattering condition to have the exactly correct boundary conditions in obtaining Φ, since the overlapping integral $\langle \varphi_{k_0} | \Phi \rangle$ in Eq. (8) will be divergent, unless they are orthogonal. This orthogonality can now be easily accomplished, by recognizing their $\pi/2$ phase difference.

Finally, we now show an analytic exercise as a demonstration of the equivalence of the matrix-element integration method and the differential equation method for scattering conditions. We assume the simple case, where

$$\begin{aligned} \phi_i = \phi_f &= \sin k_0 r \qquad \text{(i.e., } s\text{-wave)}, \\ H' &= H'' = e^{-ar} \\ H_0 &= \mathbf{P}^2/2m \qquad \text{(plane-wave)}. \end{aligned}$$

We solve the differential equation

$$\left(\frac{d^2}{dr^2} + k_0^2\right) \Phi = e^{-ar} \sin(k_0 r). \tag{9}$$

The homogeneous solution is $\phi^h = \sin(k_0 r)$. The second boundary condition implies that $\Phi \to \cos(k_0 r)$, when $r \to \infty$. Thus, we obtain the desired solution,

$$\Phi = \frac{1}{\rho^2} e^{-ar} \sin(k_0 r) + \frac{2k_0}{a} \frac{1}{\rho^2} (e^{-ar} - 1) \cos(k_0 r), \tag{10}$$

where

$$\rho^2 = a^2 + 4k_0^2.$$

Substituting Eq. (10) into Eq. (7), we obtain

$$P = \frac{k_0^2}{4a\rho^4\eta^2} (4k_0^2 - 5a^2), \tag{11}$$

where

$$\eta^2 = a^2 + k_0^2.$$

The principal value part of the integration is given by

$$\begin{aligned} P &= P \int_0^\infty \left(\frac{2}{\pi}\right) dk \, \frac{|\langle \sin(k_0 r) \mid e^{-ar} \mid \sin(kr) \rangle|^2}{k_0^2 - k^2} \\ &= \left(\frac{2}{\pi}\right)\left(\frac{a^2}{4}\right) P \int_0^\infty dk \, \frac{1}{k_0^2 - k^2} \left[\frac{1}{a^2 + (k_0 - k)^2} - \frac{1}{a^2 + (k_0 + k)^2}\right]^2. \end{aligned} \tag{12}$$

After a straightforward but lengthy manipulation (six pages in our case!), we obtain identical results as in Eq. (11).

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