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# Logarithmic perturbation expansions

C. K. Au and Y. Aharonov*
*Department of Physics and Astronomy, University of South Carolina, Columbia, South Carolina 29208*

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A method previously developed for one-dimensional nonrelativistic perturbation theory is extended to three-dimensional problems. This method essentially consists of performing the perturbation expansion on the logarithm of the wave function instead of on the wave function itself. It is shown that, for the first-order corrections in problems that are not reducible to one dimension, this method is equivalent to that of Sternheimer and to that of Dalgarno and Lewis. In the present approach, the higher-order corrections can be obtained in a hierarchical scheme and there exists an isomorphisim between the equation for the first-order correction and the equation for the $i$th-order correction. As an illustration of the technique developed, the authors consider the hydrogen atom in an external multipole field and in two different spherically symmetric perturbation potentials, $\delta(r-a)$ and $e^{-\alpha r}$. The last potential is related to the problem of the screened Coulomb potential. By considering the $\delta(r-a)$-type potential, two interesting sum rules are obtained.

## INTRODUCTION

In a previous paper[1] we have developed a new approach to nonrelativistic perturbation theory in problems reducible to one dimension. This method essentially consists of performing the perturbation expansion on the logarithm of the wave function instead of on the wave function itself. In the case of excited states in which the wave functions possess nodes, the zeros need to be located and factored out before the logarithm is taken. We have shown in Paper I that with this technique all interesting physical quantities, namely, the corrections to the wave function, energy, and the nodal positions, are expressible in exact quadrature in a hierarchical scheme, to all orders in perturbation theory. However we are unable to achieve the same results in three-dimensional problems that are not reducible to one dimension.

In this paper we extend our technique to three-dimensional problems. In doing so, we establish contact with the previous works of Sternheimer[2] and Dalgarno and Lewis,[3] whose techniques have been extensively and successfully exploited in many calculations in the past three decades.[4] As we shall show, the quantity $f(r)$ that Dalgarno and Lewis introduced in their classic paper[3] relates simply to the first-order correction to the logarithm of the wave function.

The scheme of the present paper is as follows. In Sec. I we establish the hierarchy of equations for the corrections to the energy and the logarithm of the wave function, to all orders in perturbation theory, and establish the isomorphism between the equation for the $i^{\text{th}}$ order correction and the equation for the first-order correction. In Sec. II we show that the first two equations in our hierarchy reduce to the Sternheimer equation. In Sec. III we show that our first-order equation is equivalent to the Dalgarno-Lewis equation. In Sec. IV we obtain the first-order correction to the wave function and the second-order energy shift for a hydrogen atom in an external multipole field. In Sec. V we discuss the problem of the hydrogen atom in two different spherically symmetric perturbation potentials, $\delta(r-a)$ and $e^{-\alpha r}$. We obtain two sum rules in the problem with the $\delta(r-a)$-type potential. The solution to the $e^{-\alpha r}$ potential is related to the solution of the screened Coulomb potential. Finally, in Sec. VI we make some concluding remarks.

## I. PERTURBATION SERIES ON LOGARITHM OF WAVE FUNCTION

In the present paper we only consider ground states in which the wave function contains no nodes. Along the same lines as in Paper I we define

$$\psi(x)=\exp[-G(x)]\,, \tag{1.1}$$

and

$$\vec{g}(x)=\vec{\nabla}G(x)\,. \tag{1.2}$$

Putting this into the Schrödinger equation

$$H\psi(x)=(-\tfrac{1}{2}\nabla^2+V_0+\lambda V_1)\psi=E\psi\,, \tag{1.3}$$

we obtain

$$\operatorname{div}\vec{g}-\vec{g}^{\,2}=2(E-V_0-\lambda V_1)\,. \tag{1.4}$$

As in Paper I we expand $G$, $g$, and $E$ as power series expansions in $\lambda$:

$$G=G_0+\lambda G_1+\lambda^2 G_2+\cdots\,, \tag{1.5}$$

$$\vec{g}=\vec{g}_0+\lambda\vec{g}_1+\lambda^2\vec{g}_2+\cdots\,, \tag{1.6}$$

and

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots \,, \tag{1.7}$$

where

$$\psi_0 = \exp(-G_0) \tag{1.8}$$

and $E_0$ are the unperturbed wave function and the corresponding eigenenergy. On comparing coefficients of various powers in $\lambda$ in Eq. (1.4), we have the following hierarchy of equations:

$$\operatorname{div} \vec{g}_0 - \vec{g}_0^{\,2} = 2(E_0 - V_0)\,, \tag{1.9}$$

$$\operatorname{div} \vec{g}_1 - 2\vec{g}_0 \cdot \vec{g}_1 = 2(E_1 - V_1)\,, \tag{1.10}$$

$$\operatorname{div} \vec{g}_2 - 2\vec{g}_0 \cdot \vec{g}_2 = 2(E_2 + \tfrac{1}{2}\vec{g}_1 \cdot \vec{g}_1)\,, \tag{1.11}$$

and in general for $i \geqslant 2$

$$\operatorname{div} \vec{g} - 2\vec{g}_0 \cdot \vec{g}_i = 2\left(E_i + \tfrac{1}{2}\sum_{j=1}^{i-1} \vec{g}_j \cdot \vec{g}_{i-j}\right). \tag{1.12}$$

We observe the following interesting feature in this hierarchy of equations. Equation (1.12) has the same structure as (1.10), which gives the correction to first order. Even if one cannot solve the differential equation in (1.10), one can always solve for $E_1$ and $G_1$, and hence $g_1$ by the ordinary Rayleigh-Schrödinger method. Therefore we see that the $i^{\text{th}}$ order correction to the energy and the logarithm of the wave function may be obtained as in a first-order perturbation calculation, provided that the perturbative potential $V_1$ is replaced by $-\frac{1}{2}\sum_{j=1}^{i-1}\vec{g}_j \cdot \vec{g}_{i-j}$.

## II. CONNECTION TO STERNHEIMER'S METHOD

In this section we establish the connection to Sternheimer's method.[2] First we observe that as in Paper I the square of the unperturbed wave function $\rho \equiv \psi_0^2 = \exp(-2G_0)$, constitutes an integrating factor for Eq. (1.10) and the subsequent equations in the hierarchy. Multiplying Eq. (1.10) by this factor, we get

$$\operatorname{div}(\vec{g}_1 e^{-2G_0}) = 2(E_1 - V_1)e^{-2G_0}. \tag{2.1}$$

On integrating this over all space and using Green's theorem and the fact that $\psi_0$ vanishes at infinity and is normalized, we obtain

$$E_1 = \int V_1 \rho \, d^3r\,, \tag{2.2}$$

in agreement with the ordinary Rayleigh-Schrödinger theory. Applying the same integrating factor up the hierarchy, we obtain

$$E_i = -\int \left(\tfrac{1}{2}\sum_{j=1}^{i-1} \vec{g}_j \cdot \vec{g}_{i-j}\right)\rho \, d^3r\,. \tag{2.3}$$

Next we show that Eqs. (1.10) and (1.9) together yield the Sternheimer equation.[2] We first observe the relation between the first-order correction to the logarithm of the wave function, $G_1$, and the first-order correction to the wave function, $\psi_1$. This can be obtained by expanding both sides of Eq. (1.1) in powers of $\lambda$. We get

$$\psi_1 = -G_1 e^{-G_0} = -G_1 \psi_0\,. \tag{2.4}$$

Taking the Laplacian of $G_1 e^{-G_0}$, we get

$$\nabla^2(G_1 e^{-G_0}) = \{\nabla^2 G_1 - 2\vec{\nabla}G_0 \cdot \vec{\nabla}G_1 + G_1[(\vec{\nabla}G_0)^2 - \nabla^2 G_0]\} e^{-G_0}\,. \tag{2.5}$$

On using Eqs. (1.9) and (1.10) in (2.5), we have

$$\nabla^2(G_1 e^{-G_0}) = [2(E_1 - V_1) - 2(E_0 - V_0)G_1]e^{-G_0}\,, \tag{2.6}$$

which can be rearranged to give

$$[\nabla^2 + 2(E_0 - V_0)]G_1 e^{-G_0} = 2(E_1 - V_1)e^{-G_0} \tag{2.7}$$

or

$$-[\nabla^2 + 2(E_0 - V_0)]\psi_1 = 2(E_1 - V_1)\psi_0\,, \tag{2.8}$$

which is the Sternheimer equation.

Using the isomorphism established at the end of Sec. I, we arrive at the following generalized Sternheimer equation:

$$[\nabla^2 + 2(E_0 - V_0)]G_i \psi_0 = 2(E_i - V_i)\psi_0\,, \,. \tag{2.9}$$

where $V_i$, the "effective" $i^{\text{th}}$ order perturbation potential is given by

$$V_i = -\tfrac{1}{2}\sum_{j=1}^{i-1} \vec{g}_j \cdot \vec{g}_{i-j}\,. \tag{2.10}$$

One may look upon Eqs. (1.9) and (1.10) as a means of decoupling the Sternheimer equation. This decoupling enables $g_1$, which is no longer a vector function in the case of one dimension,[1] to be integrable in exact quadrature. The first-order correction to the logarithm of the wave function, $G_1$, can be obtained by integrating this known function $g_1$. In the case of three dimensions, because of the vectorial nature of the function $\vec{g}_1 \equiv \nabla G_1$, such simple situations no longer exist and we must turn to other methods. This well be discussed in Sec. IV and V.

## III. CONNECTION TO METHOD OF DALGARNO AND LEWIS

In this section we establish the connection between our work and the work of Dalgarno and Lewis.[3] In their classic paper Dalgarno and Lewis introduced an ingenious mathematical technique that allows one to obtain certain sum rules without the use of either the Green's function or an explicit sum over the intermediate states. They showed that for a given function $\eta(r)$ the following sum rule can be written[3] (the factor of $\frac{1}{2}$ is inserted on the LHS of 3.1 because the Hartree is taken as unity here, where Dalgarno and Lewis take the Rydberg as unity in their work):

$$\frac{1}{2}\sum_{m\neq 0}\frac{\langle 0|\eta|m\rangle\langle m|\eta|0\rangle}{E_0-E_0^{(m)}} = \langle 0|f\eta|0\rangle - \langle 0|f|0\rangle\langle 0|\eta|0\rangle\,, \quad (3.1)$$

where the function $f$ satisfies an inhomogeneous second-order vector differential equation:

$$2(\vec{\nabla}f)\cdot(\vec{\nabla}\psi_0)+\psi_0(\nabla^2 f)=\eta\psi_0\,. \quad (3.2)$$

We show that $f$ is trivially related to the first-order correction to the logarithm of the wave function. Hence we shall understand why, in solving the inhomogeneous equation (3.2), the particular solution that goes to zero as $\eta$ goes to zero must be taken. In this sense we can consider part of our present work as a supplement to the work of Dalgarno and Lewis.

On dividing Eq. (3.2) on both sides by $\psi_0$, we obtain

$$(\nabla^2 f)+2(\vec{\nabla}f)\cdot\nabla(\ln\psi_0)=\eta\,. \quad (3.3)$$

From the definition of $G$ we see that

$$\vec{\nabla}\ln\psi_0=-\vec{g}_0\,. \quad (3.4)$$

For simplicity we consider the case in which the first-order energy shift $E_1$ is equal to zero, since one always has the freedom to redefine the perturbation $\eta$ as $\eta'\equiv\eta-\langle 0|\eta|0\rangle$. This transformation will leave both sides of Eq. (3.1) invariant. Under this renormalization of the perturbation, Eq. (1.10) becomes

$$\nabla^2 G_1+2\vec{\nabla}G_1\cdot\vec{\nabla}(\ln\psi_0)=-2V_1 \quad (3.5)$$

or

$$\nabla^2(-\tfrac{1}{2}G_1)+2\vec{\nabla}(-\tfrac{1}{2}G_1)\cdot\vec{\nabla}(\ln\psi_0)=V_1\,. \quad (3.6)$$

On comparing Eq. (3.3) with Eq. (3.6), we immediately identify the Dalgarno-Lewis function $f$ with $-\frac{1}{2}G_1$, which is one-half the first-order correction to the logarithm of the wave function.

Having thus established this identification, we see why the solution to the inhomogeneous equation (3.3) must vanish as the perturbation vanishes, since one should not have any correction to the unperturbed wave function in the absence of any perturbation.

## IV. H ATOM IN MULTIPOLE FIELD

Although this problem has been treated to first order by Dalgarno and Lewis, we would like to include it here for reasons that go beyond completeness. The important point is that we now have a means of directly calculating the first-order correction to the wave function, given any perturbation. By the same token, with the isomorphism that we established at the end of Sec. I, we now have a means of calculating the $i^{\text{th}}$ order correction to the logarithm of the wave function as if we are calculating the first-order correction by merely replacing $V_1$ with $-\frac{1}{2}\sum_{j=1}^{i-1}\vec{g}_j\cdot\vec{g}_{i-j}$. The $i^{\text{th}}$-order correction to the energy is computed according to Eq. (2.3).

We now consider a hydrogen atom in a $2^l$ th-order multipole field. The perturbation $V_1$ is then written as

$$V_l=Q_l r^l p_l\,. \quad (4.1)$$

The quantity $Q_l$ is a measure of the strength of this interaction. Under this perturbation, Eq. (1.10) becomes

$$\nabla^2 G_1-2\vec{\nabla}G_0\cdot\vec{\nabla}G_1+2Q_l r^l P_l=0. \quad (4.2)$$

For a hydrogen atom in its ground state,

$$G_0=r+\text{const.} \quad (4.3)$$

and hence

$$\vec{\nabla}G_0=\hat{r}\,. \quad (4.4)$$

We next see that $G_1(r)$ must be of the form $G_l(r)$ $P_l(\cos\theta)$ and so we redefine

$$G_1(\vec{r})=[R(r)/r]P_l(\cos\theta). \quad (4.5)$$

On substituting Eqs. (4.4) and (4.5) into (4.2), we obtain the following inhomogeneous equation for $R$:

$$R''-2R'-[l(l+1)/r^2]+2R/r+2Q_l r^{l+1}=0. \quad (4.6)$$

The particular solution for this equation is

$$R=Q_l[r^{l+1}/l+r^{l+2}/(l+1)]\,, \quad (4.7)$$

which goes to zero as $Q_l$ goes to zero, that is, when the perturbation is removed, as it must be. From Eq. (2.4) we have a simple analytic expression for the first-order correction to the wave function under this perturbation:

$$\psi_1=-Q_l[r^i/l+r^{l+1}/(l+1)]P_l(\cos\theta)(e^{-r}/\sqrt{\pi})\,. \quad (4.8)$$

Next we turn to the evaluation of the second-order energy shift. This is a straightforward application of Eq. (2.3). We obtain

$$E_2=-Q_l^2[(2l+2)!(l+2)/l(l+1)2^{2l+2}]. \quad (4.9)$$

This is in agreement with the earlier results of Dalgarno and Lewis,[3] Bell,[5] and the static limit of the general expression for the dynamic multipole polarizability of hydrogen obtained earlier by one of us.[6]

Having thus obtained $G_1$, we have $\vec{g}_1$ and we can proceed to calculate $G_2$ in our hierarchy, since $\vec{g}_1\cdot\vec{g}_1$ can then be replaced by a sum of multipole potentials with suitable 3-$j$ symbols. The resulting equation, which is derived from (1.11), can then be solved in the same format as Eq. (4.2), since this equation is linear. We have thus established a method to solve the hydrogen atom in an external multipole field to all orders in perturbation theory. Details of such calculations may be presented elsewhere.

## V. H ATOM IN SPHERICALLY SYMMETRIC POTENTIAL

In this section we would like to consider a hydrogen atom in a spherically symmetric potential. In this special case the Schrödinger equation, even with the inclusion of the perturbation potential, is reducible to one dimension. However, the radial equation is now defined in the interval $(0,\infty)$. We show the necessary modifications to the techniques we previously developed for the one-dimensional problem in which the Schrödinger equation is defined in the interval $(-\infty,\infty)$. We also carry out explicit calculations for spherically symmetric potentials of the type $\delta(r-a)$ and $\exp(-\alpha r)$. While superficially these potentials seem academic, the calculations we perform here can be modified to be applicable to the case in which we have a hard-core or a screened Coulomb potential. These situations are obviously interesting in the understanding of muonic atoms.

As is well known, for a hydrogen atom in a spherically symmetric potential the radial part of the wave function is separable and the normalization condition is

$$\int_0^\infty r^2\Phi_r^2\,dr=1, \tag{5.1}$$

and $r\Phi_r$ vanishes at both 0 and $\infty$. So we can write $r\Phi_r$ as $e^{-G}$ and $r\Phi_{r,0}$ as $e^{-G_0}$, where $\Phi_{r,0}$ is the unperturbed radial wave function. On expanding $G$ as a power series in $\lambda$ as before, we have

$$\ln\Phi_r=\ln\Phi_{r,0}-\lambda G_1-\lambda^2G_2+\cdots . \tag{5.2}$$

Thus all our previous results developed for the one-dimensional problem apply and perturbation calculations on $G_1$, $G_2,\ldots$ can be carried out as before. The only modifications are that the lower limit is raised from $-\infty$ to 0 and

$$\rho=e^{-2G_0}=r^2\Phi_{r,0}^2. \tag{5.3}$$

We now consider a perturbation of the form

$$V_1=\delta(r-a). \tag{5.4}$$

The first-order energy shift under this perturbation is

$$E_1=4a^2e^{-2a}. \tag{5.5}$$

Then according to Eq. (18) of Paper I we have

$$g_1(r)=G_1'(r)$$

$$=\frac{-2a^2e^{-2a}}{r^2}\{(1+2r+2r^2)-e^{2r}[1-\theta(r-a)]\}, \tag{5.6}$$

where $\theta(r-a)$ is the step function. The second-order energy shift can be calculated according to Eq. (23) of Paper I, except that the lower limit of integration is raised from $-\infty$ to 0:

$$E_2=-8a^4e^{-4a}\left(\int_0^a\frac{e^{2r}}{r^2}[(1+2r+2r^2)e^{-2r}-1]^2\,dr+\int_a^\infty\frac{(1+2r+2r^2)^2}{r^2}e^{-2r}\,dr\right) \tag{5.7}$$

$$\equiv-8a^4e^{-4a}F(a). \tag{5.8}$$

The integrals on the right-hand side of Eq. (5.7) are regular and expressible in terms of the exponential, hyperbolic sine and cosine (Chi) integrals, Ei, Shi, and Chi, with argument $a$. However, because of the number of Ei, Shi, and Chi functions involved, we prefer to leave the right-hand side of Eq. (5.7) in terms of these integrals and represent it by $F(a)$. We refer the interested reader to Gradshteyn and Ryzhik[7] for details. On comparing $E_2$ thus obtained with the usual second-order energy shift from the Rayleigh-Schrödinger theory, we obtain the following sum rule[8]:

$$\sum_{n\neq1}\frac{[R_{1S}(a)\cdot R_{nS}(a)]^2}{E_n-E_{1S}}a^4=8a^4e^{-4a}F(a), \tag{5.9}$$

where $R_{1S}(a)$ and $R_{nS}(a)$ are the radial wave functions of the ground state and the $nS$ excited states, evaluated at $a$. An equivalent form of Eq. (5.9) is

$$\sum_{n\neq1}\frac{[R_{nS}(a)]^2}{E_n-E_{1S}}=2e^{-2a}F(a). \tag{5.10}$$

One can generate a similar sum rule by considering the following perturbation:

$$V_1=\delta(r-a_2)/\rho_2-\delta(r-a_1)/\rho_1,\quad a_2>a_1, \tag{5.11}$$

where

$$\rho_1\equiv a_1^2[R_{1S}(a_1)]^2 \tag{5.12}$$

and

$$\rho_2\equiv a_2^2[R_{1S}(a_2)]^2. \tag{5.13}$$

For this perturbation, $E_1=0$ and

$$g_1(r)=e^{2r}/2r^2\quad\text{for } a_1\leq r\leq a_2 \tag{5.14}$$

$$=0,\quad\text{otherwise.}$$

Repeating the same technique that we used in obtaining Eq. (5.10), we arrive at the following sum rule[8]:

$$\frac{1}{4}\sum_{n\neq1}\frac{[e^{a_1}R_{nS}(a_1)-e^{a_2}R_{nS}(a_2)]^2}{E_{nS}-E_{1S}}$$

$$=\frac{1}{2}\int_{a_1}^{a_2}\frac{e^{2r}}{r^2}dr \tag{5.15}$$

$$=\left(\mathrm{Ei}(2a_2)-\frac{e^{2a_2}}{2a_2}\right)-\left(\mathrm{Ei}(2a_1)-\frac{e^{2a_1}}{2a_1}\right),$$

where we have explicitly expressed the result in terms of the exponential integral function[7] Ei.

Next we look at a perturbation of the form

$$V_1 = e^{-\alpha r}. \tag{5.16}$$

This particular potential is interesting because any potential of the form $\sum_{n=0}^{N}(a_n r^n)e^{-\alpha r}$ can be obtained by suitable differentiation. Moreover we observe

$$\int_0^\alpha e^{-\alpha r}\,d\alpha = \frac{1-e^{-\alpha r}}{r}, \tag{5.17}$$

which is the difference between a naked and a screened Coulomb potential. For an electron in a screened Coulomb potential one can always treat this difference as a perturbation. Thus solving the problem with the potential $V_1$ as given by Eq. (5.16) is equivalent to solving the screened Coulomb problem. With this $V_1$ the first-order energy shift is found to be

$$E_1 = 8/(2+\alpha)^3 \equiv 8/\beta^3. \tag{5.18}$$

The derivative of the first-order correction to the logarithm of the wave function, $g_1$, is found to be

$$g_1 = \frac{-4}{r^2\beta^3}\left[(1+2r+2r^2) - (1+\beta r+\tfrac{1}{2}\beta^2 r^2)e^{-\alpha r}\right], \tag{5.19}$$

where we have defined $\beta$ as $2+\alpha$. The second-order energy shift can be calculated as indicated in Paper I, and we obtain

$$E_2 = \frac{-32}{\beta^6}\int_0^\infty \frac{e^{-2r}}{r^2}\left[(1+2r+2r^2) - (1+\beta r+\tfrac{1}{2}\beta^2 r^2)e^{-\alpha r}\right]^2 dr. \tag{5.20}$$

This integral is a regular function of $\alpha$ and it can be handled by breaking the integration into two parts, $\int_0^\infty = \int_0^\epsilon + \int_\epsilon^\infty$, where $\epsilon$ is a small number. Then the integrand in the first integral can be expanded in powers of $r$ and the first integral can be performed exactly. The second integral is expressible in terms of the Whittaker function.[7] Of course this process is independent of the choice of the value of $\epsilon$. The higher-order corrections can then be obtained under the hierarchical scheme we discussed in Paper I. With these solutions expressed as a function of $\alpha$, the problem of the screened Coulomb potential can be solved by suitable integration of these solutions over the parameter $\alpha$.

## VI. CONCLUSION

In this paper we have approached nonrelativistic perturbation theory by using an expansion on the logarithm of the wave function. We have shown that, to first order, this is equivalent to the method of Dalgarno and Lewis.[3] Since the first-order correction to the wave function is equal to the product of the unperturbed wave function and the first-order correction to the logarithm of the wave function, our present method is also equivalent to that of Sternheimer.[2] On going to higher orders, we discover a hierarchical system of equations, each of which is isomorphic to the first-order equation. In the case of one dimension, as we have shown in Paper I, an integrating factor exists which enables the problem to be solvable in exact quadrature. As an illustration we have considered in Sec. V the problem of the hydrogen atom in two different spherical potentials, $\delta(r-a)$ and $e^{-\alpha r}$. By considering the former, we discover two sum rules[9] as given by Eqs. (5.10) and (5.15). As we have pointed out in Sec. V, the solution corresponding to the perturbation potential $e^{-\alpha r}$ leads, by suitable integration, to the solution corresponding to the potential $(1-e^{-\alpha r}/r)$. Thus in principle we have established a method to solve the Schrödinger equation for a charged particle in a screened Coulomb potential, which is equivalent to the Schrödinger equation for a hadron in a Yukawa-type potential. We hope to return to this discussion in a future paper.

In the case in which the perturbation does not have spherical symmetry, our treatment of the first-order correction is equivalent to that of Dalgarno and Lewis. However our work has gone beyond that of Dalgarno and Lewis in our discussion on the higher-order corrections. We have established an isomorphism between the equation for the $i^{\text{th}}$-order correction to that for the first order.

It should be noted that there also exist variational methods[10,11] in the calculation of matrix elements. In systems in which the differential equations from the Sternheimer and Dalgarno-Lewis method prove to be too difficult to solve, such variational methods may be preferred. Nevertheless the extension of these variational methods to higher orders is not trivial. It is conceivable that the isomorphism which we have established in this paper between the first-order correction and a higher-order correction would make the extension of these variational techniques to higher order less tedious. However we have not investigated its feasibility.

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[1] Y. Aharonov and C. K. Au, Phys. Rev. Lett. 42, 1582 (1979), hereafter referred to as Paper I.

[2] R. Sternheimer, Phys. Rev. 84, 244 (1951).

[3] A. Dalgarno and J. T. Lewis, Proc. R. Soc. London 233, 70 (1955).

[4] It is almost impossible to cite all the work in the literature that has made use of the Sternheimer and Dalgarno-Lewis method. This method has been exploited in all major subfields of physics. Just to mention an example, this method has been extensively utilized to calculate parity nonconservation effects in atoms due to neutral current interactions. See, for example, a review article by G. Feinberg, Nature 271, 509 (1978).

[5] R. J. Bell, Proc. Phys. Soc. London 92, 842 (1967). We would like to remind the readers that Bell uses the Rydberg as unity, whereas we use the Hartree as unity in this paper.

[6] C. K. Au, J. Phys. B 11, 2781 (1978).

[7] I. S. Gradshteyn and I. M. Byzhik, *Tables of Integrals, Series and Products* (Academic, New York, 1965).

[8] In Eq. (5.9) and (5.15) the sum over intermediate states includes the continuum.

[9] In the case of the hydrogen atom such sum rules can be regarded as mathematical curiosities. However in more complicated systems similar sum rules can be derived and used as constraints in calculations concerning the excited states.

[10] E. Gerjuoy, A. R. P. Rau, L. Rosenberg, and L. Spruch, Phys. Rev. A 9, 108 (1974).

[11] J. O. Hirschfelder, W. R. Brown, and S. T. Epstein, Adv. Quantum Chem. 1, 225 (1964). This reference discusses some general connections between perturbation theory and the variational principle.