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Multipole polarizabilities for hydrogenic bound states

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The bound-state wave function of a single nonrelativistic particle is written as $F\exp(-G)$, where F contains the nodal information and is restricted to be a polynomial and G is the negative of the logarithm of the wave-function envelope which contains the spectral information. As a perturbation is turned on, both F and G respond, but the response in G can be absorbed in F. A perturbative expansion on F and the energy leads to a hierarchy of inhomogeneous differential equations which resemble Gauss's law with a variable dielectric constant. If the perturbation is of polynomial form, one reasonably expects polynomial solutions for the perturbative corrections to F in this hierarchy. This method is used to obtain the first-order wave-function correction for the hydrogenic $2S$ and $2P_0$ states in a multipole field and their corresponding multipole polarizabilities. In the dipole case, the method is modified to treat degenerate mixing. Then the first-order correction to the wave function for an arbitrary hydrogenic bound state with azimuthal quantum number $m=0$ in a large-order multipole field where neither degeneracy mixing nor first-order energy shift occurs and its corresponding multipole polarizabilities are calculated in closed forms.

INTRODUCTION

The calculation of multipole polarizabilities of atomic states falls under the general category of atomic sum rules. An elegant method for such calculations was first suggested by Dalgarno and Lewis.[1] From the point of view of perturbation theory, one may identify the Dalgarno-Lewis method as writing the first-order perturbation correction to the wave function as a scalar function times the unperturbed wave function.[2] This scalar function is then obtained as the solution to a multidimensional inhomogeneous differential equation. Direct attempts to obtain the perturbative corrections to the wave functions as the solution of inhomogeneous multidimensional differential equations were made earlier by Schrödinger,[3] Podolsky,[4] and Sternheimer.[5] For multielectron atoms, the Z-expansion method for calculating atomic polarizabilities and shielding factors was introduced by Dalgarno and Stewart.[6] This method was later extended by Cohen[7,8] and by Cohen and Drake[9,10] to the calculations of the dipole polarizabilities of the lithium and sodium isoelectronic sequence and the dipole hyperpolarizabilities of S-state atoms and ions in the first two rows and the multipole polarizabilities of the helium isoelectronic sequence.

In this paper we are basically concerned with the wave-function corrections of hydrogenic bound states in multipole fields and their multipole polarizabilities. To obtain the corrections to the wave function we first write the bound-state wave function of a single-particle system as $F\exp(-G)$. F contains all the nodal information of the wave function and is restricted to be a polynomial. G is the negative of the logarithm of the wave-function envelope and contains the spectral information. As a perturbation is turned on, both F and G will respond. However, any response in G can be absorbed in the response in F by expansion of $\exp(-G)$. If, on the other hand, one absorbs all the corrections to $F\exp(-G)$ in G, one recovers the logarithmic perturbation-expansion method.[11] But the fact that F may contain zeros makes this not applicable for excited states. Hence, for excited-state perturbation problems, it is more convenient to absorb the corrections to G in F. As we shall show in Sec. I, if the perturbation is in the form of a polynomial, one reasonably expects polynomial solutions for the corrections in F. A perturbation expansion on F and the energy leads to a hierarchy of multidimensional inhomogeneous differential equations that have the same form as Gauss's law in electrodynamics but with a variable dielectric constant.[2,12,13] Should degeneracy occur in the unperturbed problem, the present method needs modification and additional bookkeeping of the degeneracy index. One needs to start with a basis that diagonalizes the first-order perturbation matrix. If the degeneracy is lifted in first order then the complete first-order correction to the wave function is determined by the second-order equation, as is the case in ordinary degenerate perturbation theory.[14] In Sec. II we apply the presently developed perturbation method to obtain the first-order correction to the wave function of the hydrogenic $2S$ state in a static multipole field,[15] and hence the multipole polarizabilities. In Sec. III we repeat the calculation for the $2P_0$ state. In Sec. IV we consider the Stark effect on the lowest-lying excited hydrogenic states with azimuthal quantum number $m=0$. Here the degenerate version of the present method must be used. We calculate the first- and second-order corrections to the wave function in spherical coordinates and obtain perturbation corrections to the energy to the fourth order. In Sec. V we show that the nondegenerate version of the present method may still be used to obtain "sum rules exclusive of degenerate-state contributions" by suitable use of projection operators. In Sec. VI we consider the wave-function and energy corrections of an arbitrary hydrogenic bound state (with azimuthal quantum number $m=0$) in a large-order multipole field such that neither degenerate mixing nor first-order energy shift is involved. We give the first-order correction to the wave function and hence the multipole polarizabilities in closed forms. Then in the Appendix we show how the energy shift of an atom in a rotationally invariant state, when subjected to an external potential, is related to the static multipole polarizabilities given in sum rule form by Dalgarno.[16]

I. PERTURBATION METHOD FOR MULTIDIMENSIONAL SYSTEMS

We consider the nonrelativistic Schrödinger equation for the bound states of a multidimensional single-particle system

$$\begin{aligned} H\psi &= \left[H_0 + \sum_i \lambda^i V_i(\vec{r}) \right] \psi \\ &= [-\tfrac{1}{2}\nabla^2 + V(\vec{r})]\psi \\ &= E\psi , \end{aligned} \tag{1.1}$$

where

$$H_0 = -\tfrac{1}{2}\nabla^2 + V_0(\vec{r}) \tag{1.2}$$

such that ∇^2 is the n-dimensional Laplacian operator and that $\vec{r}$ is an n-dimensional position vector. In the usual Rayleigh-Schrödinger perturbation theory, the wave function ψ is expanded in a power series of the coupling constant

$$\psi = \sum_{i=0}^{\infty} \lambda^i \psi_i \tag{1.3}$$

and the corrections to the wave function are obtained as solutions to inhomogeneous multidimensional differential equations.[5] Since the wave function is generally a complicated mathematical function, there is no reason to expect that solutions to ψ_i are of simple form.

In this paper we present a modification of the usual Rayleigh-Schrödinger perturbation theory whereby one can obtain solutions to the wave-function corrections via multidimensional differential equations for which one reasonably expects solutions in polynomial form. If the total potential $V(\vec{r})$ is sufficiently smooth, the stationary bound-state wave function can be written[17] as

$$\psi(\vec{r}) = F(\vec{r})\exp[-G(\vec{r})] , \tag{1.4}$$

where both F and G are regular functions. $F(\vec{r})$ contains the nodal structure of the wave function and is restricted to be a polynomial. $G(\vec{r})$, which may have very complicated structure, is the negative of the logarithm of the wave-function envelope and thus contains spectral information about the state ψ. The overall normalization of the wave function can be absorbed as an additive constant in G or as a multiplicative factor in F. In terms of the functions F and G, the Schrödinger equation (1.1) is transformed to Ricatti form and it involves the n-dimensional gradient of G only. Hence the overall additive constant in G is uniquely determined by the normalization. On using the transformation expressed in Eq. (1.4) in Eq. (1.1), we obtain

$$\nabla^2 F - 2\vec{\nabla}F\cdot\vec{\nabla}G - F(\nabla^2 G - \vec{\nabla}G\cdot\vec{\nabla}G) = 2F(V-E) . \tag{1.5}$$

From the structure of Eq. (1.5) one observes that if the potential terms $V_i(r)$ are given by polynomials, the restriction that $F(\vec{r})$ is a polynomial and the fact that E is a number presumably expandable in a power series in λ imply that if one expands both F and G power series in λ,

$$F = \sum_i \lambda^i F_i \tag{1.6}$$

and

$$G = \sum_i \lambda^i G_i , \tag{1.7}$$

then F_i and G_i $(i \geq 1)$ would have polynomial solutions. The zeroth-order equation corresponding to Eq. (1.5) is

$$\begin{aligned} \nabla^2 F_0 - 2\vec{\nabla}F_0\cdot\vec{\nabla}G_0 - F_0(\nabla^2 G_0 - \vec{\nabla}G_0\cdot\vec{\nabla}G_0) \\ = 2F_0(V_0 - E_0) \end{aligned} \tag{1.8}$$

and is presumed solvable, i.e., all of F_0, G_0, and E_0 are known. The corresponding first-order equation is

$$\nabla^2 F_1 - 2\vec{\nabla}F_1\cdot\vec{\nabla}G_0 - 2\vec{\nabla}F_0\cdot\vec{\nabla}G_1 - F_1(\nabla^2 G_0 - \vec{\nabla}G_0\vec{\nabla}G_0) - F_0(\nabla^2 G_1 - 2\vec{\nabla}G_0\cdot\vec{\nabla}G_1) = 2F_0(V_1 - E_1) + 2F_1(V_0 - E_0) . \tag{1.9}$$

It is quite apparent that there is too much freedom in this equation to allow for the unique determination of F_1, G_1, and E_1. However, upon using Eq. (1.8) in Eq. (1.9), Eq. (1.9) can be reduced to

$$\nabla^2(F_1 - F_0G_1) - 2\vec{\nabla}(F_0 - F_0G_1)\cdot\vec{\nabla}G_0 - (F_1 - F_0G_1)(\nabla^2 G_0 - \vec{\nabla}G_0\cdot\vec{\nabla}G_0) = 2(F_1 - F_0G_1)(V_0 - E_0) + 2F_0(V_1 - E_1) . \tag{1.10}$$

On multiplying Eq. (1.10) by F_0 and again making use of Eq. (1.9), we have

$$F_0\nabla^2(F_1 - F_0G_1) - 2F_0\vec{\nabla}(F_1 - F_0G_1)\cdot\vec{\nabla}G_0 + (F_1 - F_0G_1)\cdot(2\vec{\nabla}F_0\vec{\nabla}G_0 - \nabla^2 F_0) = 2F_0(V_1 - E_1) \tag{1.11}$$

which upon multiplication of both sides by $\exp(-2G_0)$ reduces to

$$\begin{aligned} \vec{\nabla}\cdot\{[F_0\vec{\nabla}(F_1 - F_0G_1) - (F_1 - F_0G_1)\vec{\nabla}F_0]\exp(-2G_0)\} \\ = 2F_0^2(V_1 - E_1)\exp(-2G_0) . \end{aligned} \tag{1.12}$$

From this E_1 can be obtained by integrating both sides of Eq. (1.12) and making use of Green's theorem,

$$E_1 = \int V_1 F_0^2 \exp(-2G_0) d^3r = \int V_1 \psi_0^2 d^3r , \tag{1.13}$$

which is the same as ordinary perturbation theory. With

E_1 thus obtained, Eq. (1.10) becomes a multidimensional differential equation for the function $(F_1-F_0G_1)$. If the first-order correction G_1 to the logarithm of the wave-function envelope G is of polynomial form, then $(F_1-F_0G_1)$ will have a polynomial solution since F is restricted to be a polynomial. We also note the following relation:

$$(F_0+\lambda F_1)e^{-(G_0+\lambda G_1)}=[F_0+\lambda(F_1-F_0G_1)]e^{-G_0} \tag{1.14}$$

to first order in λ. This is equivalent to saying that although both F and G respond to the perturbation to first order in λ, the response in G can be absorbed in F as if the logarithm of the wave-function envelope G stays constant in the presence of the perturbation. Similar statements can be made about the corrections of higher order in λ. Hence, one comes to realize that even though both F and G get disturbed by the perturbation, to any finite order in perturbation theory, any disturbance in G can be absorbed in F by expanding $\exp(-G)$. On the contrary, since F contains the nodal structures, the disturbance in F cannot be absorbed in G if we want both F and G to remain regular as the perturbation is turned on. Thus, one can insist that as the perturbation is introduced, only F will respond. By keeping $\vec{\nabla} G$ fixed, we are retaining as much as possible the information about the unperturbed wave function for the perturbed one. Based on the above arguments, we shall keep G constant in all perturbative calculations and write

$$\psi_0=F_0\exp(-G)\ , \tag{1.15}$$

and

$$\begin{aligned}\psi&=F\exp[-G-K(\lambda)]\\&=\left[\sum_i \lambda^i F_i\right]\exp[-G-K(\lambda)]\\&=\sum_i \lambda^i\psi_i\ ,\end{aligned} \tag{1.16}$$

where $K(\lambda)$ is the additive constant to G that is completely determined by normalization. Then the unperturbed version of Eq. (1.5) is

$$\nabla^2F_0-2\vec{\nabla}F_0\cdot\vec{\nabla}G_0-F_0(\nabla^2G-\vec{\nabla}G\cdot\vec{\nabla}G)=2F_0(V_0-E_0)\ , \tag{1.8$'$}$$

where F_0, G, and E_0 are known, and we have replaced G_0 by G since we are keeping G fixed. On expanding the energy in power series in λ

$$E=\sum_i \lambda^i E_i \tag{1.17}$$

and using this and Eq. (1.16) in Eq. (1.5), we obtain the equation for the perturbation correction to any order, which, on multiplication by F_0 on both sides and making use of Eq. (1.8′), becomes

$$F_0\nabla^2F_i-2F_0\vec{\nabla}F_i\cdot\vec{\nabla}G+F_i(2\vec{\nabla}F_0\cdot\vec{\nabla}G-\nabla^2F_0)=2F_0\left[\sum_{j=0}^{i-1}F_j(V_{i-j}-E_{i-j})\right]\ . \tag{1.18}$$

On multiplication of both sides by $\exp(-2G)$, this further reduces to

$$\vec{\nabla}\cdot\{[\vec{\nabla}(F_i/F_0)][F_0^2\exp(-2G)]\}=\left[2F_0\left[\sum_{j=0}^{i-1}F_j(V_{i-j}-E_{i-j})\right]\right]\exp(-2G) \tag{1.19}$$

which resembles Gauss's law in classical electrodynamics. However, one may not directly borrow the solution from electrodynamics because the left-hand side of Eq. (1.19) cannot be written as the Laplacian of a scalar function. Hence Eq. (1.19) is Gauss's law with a variable dielectric constant.[2,12,13] Equation (1.19) is in hierarchical form and each equation in this hierarchy is isomorphic to the first-order equation upon the identification

$$V_i^{\text{eff}}=V_i+\sum_{j=1}^{i-1}F_j(V_{i-j}-E_{i-j})/F_0 \tag{1.20}$$

as the effective ith-order perturbation for $i\geq 2$. With this identification, Eq. (1.19) can be written in the general form

$$\vec{\nabla}\cdot[\psi_0^2\vec{\nabla}(F_i/F_0)]=2(V_i^{\text{eff}}-E_i)\psi_0^2\ ,\quad i\geq 1\ . \tag{1.21}$$

On integrating over all of the n-dimensional space and using the divergence theorem and the fact that ψ_0^2 vanishes at infinity, we have

$$E_i=\int V_i^{\text{eff}}\psi_0^2d^3r\ ,\quad i\geq 1\ . \tag{1.22}$$

With E_i thus found, F_i is determined by the multidimensional differential equation (1.21). The factor (F_i/F_0) in the left-hand side of Eqs. (1.19) and (1.21) can be identified as (ψ_i/ψ_0) on multiplying both numerator and denominator by the same factor $\exp(-G)$ and ignoring the order-by-order renormalization constant $K(\lambda)$. This is possible since only the gradient of G enters into the Ricatti-type equation (1.5) and $K(\lambda)$ is purely an additive renormalization constant to G. In this case, one must identify the normalization used at the end of each perturbation step in the usual way, namely, either require $\langle\psi_0\,|\,\psi_i\rangle=0$ for all i or require the partial sum of the perturbative series of the wave function be normalized to unity, that is,

$$\langle\psi^{(N)}\,|\,\psi^{(N)}\rangle=1\ , \tag{1.23}$$

where

$$\psi^{(N)}\equiv\sum_{i=0}^{N}\lambda^i\psi_i\ . \tag{1.24}$$

Then Eq. (1.13) can be rewritten as

$$\vec{\nabla}\cdot[\psi_0^2\vec{\nabla}(\psi_i/\psi_0)]=2(V_i^{\text{eff}}-E_i)\psi_0^2\ . \tag{1.25}$$

For $i=1$, this can be identified with the equation obtained by Hirschfelder *et al.*[2,18] Except for the ground state where the wave function does not contain any zeros, the factor (F_i/F_0), or equivalently (ψ_i/ψ_0), is singular at the nodal points or nodal surfaces of the unperturbed wave function in cases of excited states. Thus, in general, in the procedures where one identifies ψ_i/ψ_0 as a scalar function Φ_i, one does not expect to obtain regular function solutions to Φ_i. However, by turning to Eq. (1.18) rather than Eq. (1.25) one has better hopes of finding regular solutions for F_i. In a sense this is equivalent to saying that since one expects ψ_i to be singular at the nodal surfaces of ψ_0, one may as well guess the solution for ψ_i to be F_i/F_0. Nevertheless, even if one has the option to choose to solve either Eq. (1.18) or (1.25), in practice it is the equation in the form of (1.18) that is easier to solve. This is particularly true if the perturbations V_i are given as a sum of multipole terms and the unperturbed functions F_0 and G can be expanded in terms of a finite number of spherical harmonics. The latter requirement is met in all bound-state problems arising from an initial "unperturbed" central potential. The former is usually the case in most atomic calculations of interest. Then F_i can be expanded in spherical harmonics and the projections of Eq. (1.18) on different spherical harmonics become coupled ordinary differential equations whose source terms are polynomials. In this case one reasonably expects polynomial solutions for the function F_i. The method presented here is applicable, but not limited, to hydrogenic problems. Great simplification occurs when G is a function of the radial distance r only. Here, the projection on each spherical harmonic manifold decouples from other projections, resulting in ordinary second-order differential equations. This is true in hydrogenic problems and is expected to be true for all unperturbed central force problems.

We have argued in the above that any perturbative correction to G can be absorbed in F by expanding the exponent. In realistic situations where the total physical potentials, including the perturbation, vanish at infinity, the logarithm of the wave-function envelope G is determined by its asymptotic behavior, which in nonrelativistic problems goes like $\sqrt{2mE}\,r$. Thus one can use this asymptotic property to adjust G. For example, let us assume that one has successfully carried out the present perturbation scheme to order N, i.e., one knows E_i and F_i for $i=0,\ldots,N$. One defines

$$G^{(N)}\equiv\sum_{j=0}^{N}\lambda^i\frac{\partial}{\partial\lambda^j}\left[\sqrt{2mE_0}\,r\left[1+\frac{1}{E_0}\sum_{i=1}^{N}\lambda^iE_i\right]^{1/2}\right], \tag{1.26}$$

where in realistic problems we expect

$$G^{(0)}=G\ , \tag{1.27}$$

and then defines an adjusted $F^{(N)}$ through the relation

$$\left[\sum_{i=0}^{N}\lambda^iF_i\right]e^{-G}\equiv F^{(N)}e^{-G^{(N)}} \tag{1.28}$$

up to order N, where the exponential factor on the right-hand side is expanded in power series and truncated at N and then $F^{(N)}$ is determined by comparing powers of λ on both sides.

Should degeneracy arise in the unperturbed problem, as in the nonrelativistic hydrogenic problem without spin, the present method needs to be modified. For simplicity we shall assume that V_i vanishes for $i\geq 1$ and that degeneracy is lifted in first order. In the case of an unperturbed central potential that vanishes asymptotically, as in the hydrogenic problem, G is spectroscopically determined. Hence the degenerate states can be chosen to have the same G. On denoting the degenerate states with a superscript α ($\alpha=1,\ldots,g$, where g is the degree of degeneracy), the wave function and its energy can be written as

$$\begin{aligned}\psi^\alpha&=F^\alpha\exp(-G)\\&=\left[\sum_i\lambda^iF_i^\alpha\right]\exp(-G)\ ,\end{aligned} \tag{1.29}$$

and

$$E^\alpha=\sum_i\lambda^iE_i^\alpha\ , \tag{1.30}$$

where

$$E_0^\alpha=E_0^\beta=E_0\ \ \text{for }\alpha,\beta=1,\ldots,g \tag{1.31}$$

and

$$E_1^\alpha=\langle\alpha\,|\,V_1\,|\,\alpha\rangle\neq\langle\beta\,|\,V_1\,|\,\beta\rangle=E_1^B\ \ \text{for }\alpha\neq\beta\ . \tag{1.32}$$

In writing Eq. (1.32) we have assumed that we have chosen suitable orthonormal combinations of the degenerate states to diagonalize the perturbation matrix and that degeneracy is lifted in first order.[14] Equation (1.8′) can be rewritten with the degeneracy index

$$\nabla^2F_0^\alpha-2\vec{\nabla}F_0^\alpha\cdot\vec{\nabla}G=F_0^\alpha[2(V_0-E_0)+\nabla^2G-\vec{\nabla}G\cdot\vec{\nabla}G] \tag{1.33}$$

and Eq. (1.18) can be rewritten as

$$F_0^\beta\nabla^2F_i^\alpha-2F_0^\beta\vec{\nabla}F_i^\alpha\cdot\vec{\nabla}G-F_i^\alpha(\nabla^2F_0^\beta-2\vec{\nabla}F_0^\beta\cdot\vec{\nabla}G)=2F_{i-1}^\alpha F_0^\beta V_1-2\sum_{j=1}^{i-1}F_j^\alpha F_0^\beta E_{i-j}^\alpha-2F_0^\alpha F_0^\beta E_i^\alpha\ , \tag{1.34}$$

where Eq. (1.33), with $\alpha\leftrightarrow\beta$, has been used. On multiplication of both sides by $\exp(-2G)$, the degenerate analog of Eq. (1.19) can be obtained:

$$\vec{\nabla}\cdot[(F_0^\beta\vec{\nabla}F_i^\alpha-F_i^\alpha\vec{\nabla}F_0^\beta)\exp(-2G)]=2\left[F_0^\beta\left[F_{i-1}^\alpha V_1-\sum_{j=1}^{i-1}F_j^\alpha E_{i-j}^\alpha-F_0^\alpha E_i^\alpha\right]\right]\exp(-2G)\ . \tag{1.35}$$

Equation (1.35) allows us to determine the amount of mixing of F_0^β into F_i^α. First, we notice that any F_0^α is a homogeneous solution to the differential equation (1.34). Incidentally, the same is true in the nondegenerate case. But here the mixing is completely determined by the normalization of the perturbed wave function. Let us, for the moment, choose our normalization so that

$$\langle F_0^\alpha\,||F_i^\alpha\rangle\equiv\langle\psi_0^\alpha\,|\,\psi_i^\alpha\rangle=\int F_0^\alpha F_i^\alpha\exp(-2G)d^3r=\delta_{i0} \tag{1.36}$$

and assume that a particular solution, $F_i'^{\,\alpha}$, to the inhomogeneous differential equation (1.34) has been found such that

$$\langle F_0^\beta || F_i'^{\,\alpha} \rangle = 0 \quad \text{for } \beta = 1, \ldots, g \; . \tag{1.37}$$

The correct ith-order correction to F^α is written as

$$F_i^\alpha = F_i'^{\,\alpha} + \sum_{\gamma(\neq\alpha)} b_\gamma^\alpha(i) F_0^\gamma \; . \tag{1.38}$$

The coefficients $b_\gamma^\alpha(i)$'s are determined by the ith-order equation[19] in the hierarchy of Eq. (1.35) by integrating both sides. Using Eqs. (1.36) and (1.32) and the fact $\langle F_0^\alpha || F_0^\beta \rangle = \delta_{\alpha\beta}$, one obtains

$$b_\gamma^\alpha(i) = \frac{-\sum\limits_{j=1}^{i-1} b_\gamma^\alpha(j) E_{i-j+1}^\alpha - \int F_i'^{\,\alpha} V_1 F_0^\gamma \exp(-2G) d^3r}{E_1^\gamma - E_1^\alpha} \; . \tag{1.39}$$

Thus, Eq. (1.34) together with Eqs. (1.37)–(1.39) and the normalization condition (1.36) will determine F_i^α. If the normalization is chosen to be different from Eq. (1.36), then an appropriate amount of F_0^α must be mixed into F_i^α. An example is given in a later section.

II. METASTABLE H ATOM IN A MULTIPOLE FIELD

In this section we consider the metastable hydrogen atom in a static multipole field[15] by using the technique developed in Sec. I. Since Eq. (1.19) is linear in the function F_i, the present method applies even to the situation of a linear combination of static multipole fields where one simply has to superpose the solutions for the individual multipole. If the initial linear combination of multipoles contains a dipole field, the degenerate method discussed at the end of Sec. I must be used. We shall consider this situation in a later section.

We consider an initial perturbation of the form

$$V_1 = Q_{Ll} r^L P_l \; , \quad l \neq 1 \; , \tag{2.1}$$

where Q_{Ll} is just a number and P_l is the lth-order Legendre polynomial and $L \geq l$. We write the solution F_1 in the form

$$F_1 = \frac{1}{2[2(2l+1)]^{1/2}} R_{Ll}(r) Y_l^0 \; , \tag{2.2}$$

where $R_{Ll}(r)$ is a polynomial. For the metastable $2S$ state of hydrogen, we have

$$G^{2S} = r/2 \tag{2.3}$$

and

$$F_0^{2S} = (2-r) \frac{1}{2(2)^{1/2}} Y_0^0 \; . \tag{2.4}$$

Then the first-order correction to the energy is

$$\begin{aligned} E_1^{2S} &= \int V_1 \psi_{2S} d^3r \\ &= A_L \delta_{l0} = A_L \delta_{l0} P_l \; , \end{aligned} \tag{2.5}$$

where

$$A_L = \frac{(L+2)!}{8} (L^2 + 3L + 4) Q_{L0} \; . \tag{2.6}$$

On substituting Eqs. (2.1)–(2.6) into (1.18) for $i=1$, we obtain

$$\begin{aligned} r^2 R_{Ll}'' + R_{Ll}' r(2-r) + R_{Ll}[r - l(l+1)] \\ = 2r^2(2-r) Q_{Ll}(r^L - A_L \delta_{l0}) \; , \end{aligned} \tag{2.7}$$

where the prime indicates a derivative with respect to its argument. We next seek a power-series solution for R_{Ll}:

$$R_{Ll} = \sum_n a_n^{Ll} r^n \; . \tag{2.8}$$

On substituting Eq. (2.8) into (2.7) we obtain the following indicial equation:

$$(n+l+1)(n-l) a_n^{Ll} - (n-2) a_{n-1}^{Ll} = 2Q_{Ll}[2\delta_{n,L+2} - \delta_{n,L+3} + A_L \delta_{l0}(\delta_{n3} - 2\delta_{n2})] \; . \tag{2.9}$$

For $l=1$ a polynomial solution for R_{Ll} cannot be found. This is due to the dipole mixing of the degenerate $2S$ and $2P$ states, giving rise to unnormalizable solution for the perturbed wave function. The exclusion of this degenerate mixing by use of projection operator is discussed in a later section. For $l \neq 1$ a polynomial solution can be found:

$$a_{L+2}^{Ll} = \frac{2Q_{Ll}}{L+1} \; ,$$

$$a_n^{Ll} = \frac{2Q_{Ll}(n-2)!}{(n+l+1)!(n-l)!} \frac{(L+l+2)!(L-l+1)!}{L!} \times \left[\frac{(L+l+3)(L-l+2)}{L+1} - 2 \right]$$

$$\text{for } L+1 \geq n \geq l + \delta_{l2} + 3\delta_{l0} \; ,$$

and

$$a_2^{Ll} = -\frac{Q_{Ll}}{12}(L+2)!(L^2+3L+4)\delta_{l0} + \frac{2Q_{Ll}}{5!} \frac{(L+4)!}{L(L+1)} (L^2+3L-2)\delta_{l2} \; ,$$

and

$$a_n^{Ll} = 0 \quad \text{for all other } n \; . \tag{2.10}$$

The unperturbed solution F_0 is a solution to the homogeneous equation. The mixing of F_0 in $F_i (i \geq 1)$ is determined by the normalization condition. Once F_1 is obtained, F_2 can be found from the solution to Eq. (1.18), together with the normalization condition. The higher-order corrections are obtained by solving indicial equations similar to Eq. (2.7).

The static 2^L-order multipole polarizability for an atom in the state $|\phi\rangle$ is given by Dalgarno[16] in the sum-rule form

$$\alpha^{\phi}_{2L} \equiv 2\sum_{n} \frac{|\langle \phi | r^L P_L | n \rangle|^2}{E_0^{(n)} - E_0^{(\phi)}} , \tag{2.11}$$

where $E_0^{(n)}$ is the unperturbed energy of the state $|n\rangle$. The expression on the right-hand side of Eq. (2.11) can be identified as the second-order energy shift $E_2^{(\phi)}$ for the state $|\phi\rangle$ multiplied by -2 due to the interaction expressed in Eq. (2.1) for $L=l$. Thus the static 2^L-order multipole polarizability of metastable hydrogen can be obtained by finding E_2 for the case $L=l$ by using the method discussed in Sec. I. In general, the second-order energy shift, when an atom in a rotationally invariant state $|\phi\rangle$ is subjected to an external electrical potential ϕ, is related to the 2^L-order static multipole polarizability in the following way:

$$\Delta E^{\phi}_{(2)} = -\sum_{L} \tfrac{1}{2}\alpha^{\phi}_{2L} |\partial_{i_1} \cdots \partial_{i_L} \Phi(0)|^2 \frac{2^L}{(2L)!} , \tag{2.12}$$

where

$$\partial_{i_1} \cdots \partial_{i_L} \Phi(0) = \frac{\partial}{\partial x_{i_1}} \cdots \frac{\partial}{\partial x_{i_L}} \Phi \bigg|_{\text{center of atom}} , \tag{2.13}$$

and repeated indices are summed over. A proof of Eq. (2.12) is given in the Appendix.

According to Eqs. (1.20) and (1.22), the second-order energy shift is

$$E_2 = \int F_0 F_1 V_1 \exp(-2G) d^3r . \tag{2.14}$$

For $L=l$, $L \geq 2$, according to Eq. (2.10), we have

$$R_{LL}(r) = r^L \left[\frac{2}{L+1} r^2 + \frac{4(L+2)}{L(L+1)} r + \frac{8(L+2)}{L(L-1)} \right] . \tag{2.15}$$

Substituting Eqs. (2.15), (2.2), (2.4), (2.3), and (2.1) for $L=l$ into Eq. (2.14), we obtain

$$E_2^{2S} = -2\frac{(2L-1)!(L+2)}{(L-1)}(4L^4+12L^3+7L^2-7L-4) . \tag{2.16}$$

Thus according to Eq. (2.1), the static 2^L order multipole polarizability ($L \geq 2$) is

$$\alpha^{(2S)}_{2L} = 4\frac{(2L-1)!(L+2)}{(L-1)}(4L^4+12^3+7L^2-7L-4) . \tag{2.17}$$

This agrees with the static limit of the dynamic multipole polarizability of metastable hydrogen previously evaluated with the frequency-dependent Coulomb-Green's function method.[20,19]

III. HYDROGENIC $2P_0$ STATE IN A MULTIPOLE FIELD

In this section we repeat the calculations in Sec. II for the hydrogenic $2P_0$ state. To minimize the notation we henceforth drop the subscript $m=0$ for the azimuthal quantum number. Again, we consider an initial perturbation of the form V_1 expressed in Eq. (2.1). For the $2P$ state we have

$$G^{2P} = r , \tag{3.1}$$

and

$$F_0^{2P} = \frac{r}{2(6)^{1/2}} Y_1^0 . \tag{3.2}$$

The first-order energy correction is

$$\begin{aligned} E_1^{2P} &= \int V_1 \psi^2_{2P} d^3r \\ &= \frac{(L+4)!}{24}(\sqrt{1/3}\delta_{l0} + \sqrt{4/15}\delta_{l2}) \left[\frac{3}{2l+1} \right]^{1/2} . \end{aligned} \tag{3.3}$$

On using Eqs. (3.2) and (2.1) and spherical harmonics addition rules, we have

$$F_0^{2P} V_1 = \frac{r^{L+1}}{2(6)^{1/2}} \left[\frac{3}{2l+1} \right]^{1/2} \left[\left[\frac{(l+1)^2}{(2l+1)(2l+3)} \right]^{1/2} Y^0_{l+1} + \left[\frac{l^2}{(2l+1)(2l-1)} \right]^{1/2} Y^0_{l-1} \right] . \tag{3.4}$$

We therefore seek the solution of F_1^{2P} in the form

$$F_1^{2P} = \left[\frac{1}{8(2l+1)} \right]^{1/2} \left[\left[\frac{(l+1)^2}{(2l+1)(2l+3)} \right]^{1/2} R_{Ll} Y_{l+1} + \left[\frac{l^2}{(2l+1)(2l-1)} \right]^{1/2} S_{L,l} Y^0_{l-1} \Theta(l-2) \right] , \tag{3.5}$$

where Θ is the usual step function. Upon substituting Eqs. (3.3)—(3.5) into Eq. (1.18), we have

$$r^2R'' + r(2-r)R' + [r-(l+2)(l+1)]R = 2r^{L+3} - \frac{(L+4)!}{12} r^3 \delta_{l0} \tag{3.6}$$

and

$$r^2S'' + r(2-r)S' + [r-l(l-1)]S = 2r^{L+3} - \frac{(L+4)!}{12} r^3 \delta_{l2} , \tag{3.7}$$

where we have dropped the subscript L,l from R and S. Then on writing R and S in power-series expansions

$$R = \sum_n a_n r^n \tag{3.8}$$

and

$$S = \sum_n b_n r^n , \tag{3.9}$$

we obtain the following indicial equations and their corresponding solutions for a_n and b_n:

$$(n+l+2)(n-l-1)a_n-(n-2)a_{n-1}=2\delta_{n,L+3}-\frac{(L+4)!}{12}\delta_{l0}\delta_{n3} \tag{3.10}$$

and

$$(n+l)(n-l+1)b_n-(n-2)b_{n-1}=\left[2\delta_{n,L+3}-\frac{(L+4)!}{12}\delta_{l2}\delta_{n3}\right]\Theta(l-2) \tag{3.11}$$

whose solutions are

$$a_n=\begin{cases}\dfrac{-2(n-2)!}{(n+l+2)!(n-l-1)!}\dfrac{(L+l+4)!(L-l+1)!}{(L+1)!} & \text{for } l+1+1\delta_{l0}\le n\le L+2\\ 0 \text{ otherwise}\end{cases} \tag{3.12}$$

and

$$b_n=\begin{cases}\dfrac{-2(n-2)!}{(n+l)!(n-l+1)!}\dfrac{(L+l+2)!(L-l+3)!}{(L+1)!}\Theta(l-2) & \text{for } l-1+2\delta_{l2}\le n\le L+2\\ 0 \text{ otherwise}\,.\end{cases} \tag{3.13}$$

Again for $l=1$ no polynomial solution can be found for R. The reason is the same as that in the $2S$ case where the dipole interaction causes a degenerate mixing. Having obtained the first-order wave function, one may proceed to calculate the multipole polarizability $(L\ge 2)$

$$\alpha_{2L}^{2P}=\frac{(2L+4)!}{2(2L+1)^2}\left[\left[\frac{(2L+5)}{(L+1)}\frac{(L+1)^2}{(2L+3)}+\frac{L^2}{(2L-1)}\right]+\frac{2(L+2)(L+1)}{L(2L+3)}+\frac{6L}{(2L-1)}\right]$$
$$+\frac{6L^2(2L+2)!\theta(L-3)}{(L-1)(2L-1)(2L+1)}\left[\frac{(2L+3)}{L}+\frac{2}{(L-2)}\right], \tag{3.14}$$

where the second term without the square bracket has contributions from multipoles beyond the octupole. This is because the quadrupole interaction produces a nonzero first-order energy shift for the $2P$ state, which in turn causes the recurrence relation in the indicial equation (3.11) to terminate earlier.

IV. FIRST EXCITED STATES OF HYDROGEN IN A DIPOLE FIELD

In Secs. II and III, we have explicitly avoided the dipole perturbation

$$V_1=rP_1\,. \tag{4.1}$$

This is because this particular interaction causes mixing among the degenerate $2S$ and $2P_0$ states, making it necessary to use the degenerate method discussed at the end of Sec. I. The dipole interaction causes no degeneracy difficulty for the $2P_\pi$ states. It is well known that the hydrogenic Stark effect is separable in parabolic coordinates and high-order perturbative corrections to the energies of excited states have previously been given.[21,22] However, as an illustration of the degenerate method, we shall carry out our perturbation calculation in spherical coordinates for the $m=0$ states. The perturbation in Eq. (4.1) does not mix them with $m\neq 0$ states. Under this restriction $(m=0)$, the degenerate subspace is spanned by only two states: the $2S$ and $2P_0$ (designated $2P$ for short) states. According to the discussion in Sec. I, we choose suitable combinations of the degenerate states that diagonalize the perturbation matrix:

$$|\pm\rangle=\frac{1}{(2)^{1/2}}(|2S\rangle\pm|2P\rangle)\,, \tag{4.2}$$

and in accordance with Eq. (1.4)

$$\psi^{\pm}(r)=F^{\pm}\exp(-G)=F^{\pm}\exp(-r/2)\,. \tag{4.3}$$

To zeroth order the functions $F_0^{\pm}$ are given by

$$F_0^{\pm}=\left[\frac{1}{2}\left[1-\frac{r}{2}\right]Y_{00}\pm\frac{1}{4(3)^{1/2}}rY_{10}\right]\,. \tag{4.4}$$

The first-order corrections to the energies are

$$E_1^{\pm}=\mp 3 \text{ a.u.} \tag{4.5}$$

and the first-order corrections $F_1^{\pm}$ are obtained by first finding the special solutions $F_1'^{\pm}$ to Eq. (1.34) for $i=1$ such that $F_1'^{\pm}$ is orthogonal to $F_0^{\pm}$ in accordance with Eq. (1.37). Equation (1.34) can be written in the equivalent form

$$\nabla^2F_i^{\alpha}-2\vec{\nabla}F_i^{\alpha}\cdot\vec{\nabla}G-F_i^{\alpha}[2(V_0-E_0)+\nabla^2G-\vec{\nabla}G\cdot\vec{\nabla}G]$$
$$=2\left[F_{i-1}^{\alpha}V_i-\sum_{j=0}^{i-1}F_j^{\alpha}E_{i-j}^{\alpha}\right]\,. \tag{4.6}$$

On writing the solution to Eq. (4.6), for $i=1$, as

$$F_1^\alpha = F_1'^{\alpha} + \sum_{\gamma\,(\neq\alpha)} b_\gamma^\alpha(1) F_0^\gamma \,, \tag{4.7}$$

one obtains after some straightforward calculations

$$F_1'^{\pm} = \frac{1}{4}\left[\frac{Y_{10}}{(3)^{1/2}}(r^3-30r) \pm \frac{Y_{00}}{3}(6r^2-r^3-12+6r) \mp \frac{2Y_{20}}{3(5)^{1/2}}(r^3+6r^2) \right] . \tag{4.8}$$

The projections of $F_1'^{\pm}$ on Y_{00} and Y_{10} have previously been obtained by Cohen,[7,23] and that on Y_{20} has been obtained by Cohen and Drake.[10] The coefficients $b_\gamma^\alpha(1)$ are then found according to Eq. (1.39):

$$b_-^+(1) = -b_+^-(1) = -4 \,. \tag{4.9}$$

Thus, the first-order Stark-effect corrections to the lowest excited hydrogenic state with $m=0$ under the normalization condition $\langle \psi_0 | \psi_1 \rangle = 0$, are

$$\psi_1^\pm = F_1^\pm \exp(-r/2) \,, \tag{4.10}$$

where

$$F_1^\pm = \mp \frac{Y_{00}}{12}(r^3-6r^2-18r+36) + \frac{Y_{10}}{4(3)^{1/2}}(r^3-26r) \mp \frac{Y_{20}}{6(5)^{1/2}}(r^3+6r^2) \,. \tag{4.11}$$

Knowing the first-order correction to the wave functions, one can calculate the second- and third-order corrections to the energies

$$E_2^\pm = \langle \psi_0^\pm V_1 \psi_1^\pm \rangle = -84 \text{ a.u.} \tag{4.12}$$

and

$$E_3^\pm = \langle \psi_1^\pm (V_1 - E_1^\pm) \psi_1^\pm \rangle = \mp 1560 \text{ a.u.} \tag{4.13}$$

Next, we proceed to calculate the second-order correction to the wave function subject to the normalization condition $\langle \psi_0^\pm | \psi_2^\pm \rangle = 0$. Using Eqs. (4.11), (4.12), (4.5), and (4.1), the right-hand side of Eq. (4.6) is found to be

$$F_1^\pm(V_1-E_1^\pm) - F_0^\pm E_2^\pm = \frac{Y_{00}}{12}(r^4-3r^3-8r^2-198r+396) + \frac{Y_{20}}{6(5)^{1/2}}(r^4-3r^3-44r^2) \mp \frac{Y_{10}}{60(3)^{1/2}}(9r^4-51r^3-90r^2+90r) \mp \frac{Y_{30}}{10(7)^{1/2}}(r^4+6r^3) \,. \tag{4.14}$$

The special solutions to Eq. (4.6) for $i=2$ are found to be

$$F_2'^{\pm} = \mp \frac{Q}{5(7)^{1/2}} Y_{30} + \frac{R}{3(5)^{1/2}} Y_{20} \mp \frac{S}{30(3)^{1/2}} Y_{10} + \frac{T}{6} Y_{00} \,, \tag{4.15}$$

where

$$Q = -(\tfrac{1}{4}r^5 + \tfrac{7}{2}r^4 + 14r^3) \,, \tag{4.15'}$$

$$R = -(\tfrac{1}{4}r^5 + r^4 - 15r^3 - 90r^2) \,, \tag{4.15''}$$

$$S = -(\tfrac{9}{4}r^5 + 4r^4 - 9r^3 - 4350r) \,, \tag{4.15'''}$$

and

$$T = -(\tfrac{1}{4}r^5 + \tfrac{3}{2}r^4 + 11r^3 - 66r^2 - 1686r + 3372) \,. \tag{4.15''''}$$

The coefficients $b_\gamma^\alpha(2)$ are then found according to Eq. (1.39):

$$b_-^+(2) = b_+^-(2) = 176 \,. \tag{4.16}$$

Using this normalization $E_3^\pm$ can be found:

$$\begin{aligned} E_3^\pm &= \langle \psi_0^\pm V_1 \psi_2^\pm \rangle \\ &= \int F_0^\pm V_1 F_2^\pm \exp(-r) d^3r \\ &= \int F_0^\pm V_1 F_2'^{\pm} \exp(-r) d^3r \\ &= \mp 1560 \text{ a.u.} \end{aligned} \tag{4.17}$$

in agreement with the result expressed in Eq. (4.13) and

$$F_2^\pm = F_2'^{\pm} + 176 F_0^\mp \,. \tag{4.18}$$

Instead of choosing the normalization $\langle \psi_i^\alpha | \psi_0^\alpha \rangle = 0$ for $i \neq 0$, one may choose to normalize the corrections as

$$\sum_{j=0}^{i} \langle \bar\psi_j^\alpha | \bar\psi_{i-j}^\alpha \rangle = 0 \,, \quad i > 0 \,, \tag{4.19}$$

where a bar has been written above the wave function to indicate a different normalization. Under this normalization, we have

$$\bar\psi_1^\pm = \psi_1^\pm \,, \tag{4.20}$$

and

$$\bar\psi_2^\pm = \bar F_2^\pm \exp(-r/2) \,, \tag{4.21}$$

where

$$\bar F_2^\pm = F_2^\pm - 574 F_0^\pm \,. \tag{4.22}$$

It is well known[2,24,25] that one can calculate the $(2i+1)$th-order energy correction if one knows the ith-order correction to the wave function. For example, the fourth-order energy correction is given by

$$E_4^\pm = \langle \bar\psi_1^\pm | (V_1 - E_1^\pm) | \bar\psi_2^\pm \rangle - E_2^\pm \langle \bar\psi_2^\pm | \psi_0^\pm \rangle \,, \tag{4.23}$$

where the wave-function corrections are normalized according to Eq. (4.19). Direct substitution of Eqs. (4.23), (4.21), (4.20), (4.11), (4.12), and (4.5) into Eq. (4.23) yields

$$E_4^\pm = -257\,856 \text{ a.u.} \tag{4.24}$$

This is in agreement with the value given by Alliluev *et al.*[22] The present example of the Stark effect on the lowest $m=0$ hydrogenic excited states should have illustrated how the present method applies to degenerate perturbation problems. To our knowledge, perturbative calculation to this order has never been done in spherical coordinates for this particular problem.

V. SUM RULES EXCLUSIVE OF DEGENERATE-STATE CONTRIBUTIONS

A reason why Eq. (1.18) cannot be used in degenerate perturbation theory is simply that degenerate-state contributions in the Green's function lead to vanishing energy denominators. Proper choice of linear combinations of the degenerate states that diagonalize the perturbation V_1 ensures that such singularities would not occur.[7] Similarly, one can argue that by multiplying V_1 with projection operators so as to exclude degenerate-state contributions, finite perturbative correction to the wave function should be obtained, even without first going to a basis that diagonalize V_1. In this case, one replaces V_1 by

$$V_1 \rightarrow V_1' \equiv V_1 \left[1 - \sum_{\gamma\,(\neq\alpha)} |\gamma\rangle\langle\gamma| \right] , \tag{5.1}$$

where the sum over γ is taken over the degenerate subspace.[7,26] Following the arguments that precede Eq. (1.29), one chooses to have the same G for all the states in the degenerate subspace. Then an analog of Eqs. (1.18) and (1.34) for $i=1$ can be obtained:

$$\nabla^2 F_1^{(\alpha)} - 2\vec{\nabla} F^{(\alpha)}\cdot\vec{\nabla} G - F_1^{(\alpha)}[2(V_0-E_0)+\nabla^2 G - \vec{\nabla} G\cdot\vec{\nabla} G] = 2\left[V_1 F_0^\alpha - \sum_\gamma{}' \langle\gamma | V_1 | \gamma\rangle F_0^\gamma \right] , \tag{5.2}$$

where the first-order correction is indicated by $F_1^{(\alpha)}$, the bracket around α indicating that degenerate-state contributions are excluded, and that the sum $\sum_\gamma'$ is taken over the entire degenerate subspace, including the state α. Once again, the unperturbed function F_0^α is a solution to the homogeneous equation and the particular solution must be chosen to be orthogonal to it.

For the hydrogen $2S$ and $2P_0$ states under an electric dipole perturbation, one finds, on choosing G to be $r/2$, after some straightforward calculations, that[7,10]

$$F_1^{(2S)} = \frac{1}{2(6)^{1/2}}(r^3-30r)Y_{10} , \tag{5.3}$$

and

$$F_1^{(2P)} = \left[\frac{1}{(3)^{1/2}}(6r^2-r^3-12+6r)Y_{00} - \frac{2}{(15)^{1/2}}(r^3+6r^2)Y_{20} \right] \frac{1}{2(6)^{1/2}} . \tag{5.4}$$

From these results the static dipole polarizability of the hydrogenic $2S$ and $2P$ states can be obtained:

$$\alpha^{2S} = -2\int F_0^{2S} F_1^{(2S)} r P_1 \exp(-r) d^3 r = 120 \text{ a.u.} , \tag{5.5}$$

and

$$\alpha^{2P} = -2\int F_0^{2P} F_1^{(2P)} r P_1 \exp(-r) d^3 r \equiv \alpha^{2P}(S) + \alpha^{2P}(P) , \tag{5.6}$$

where $\alpha^{2P}(S)$ and $\alpha^{2P}(D)$ are the contributions from the S state and D state portions of $F_1^{(2P)}$ in Eq. (5.4). A direct calculation leads to

$$\alpha^{2P}(D) = 208 \text{ a.u.} \tag{5.7a}$$

and

$$\alpha^{2P}(S) = 8 \text{ a.u.} , \tag{5.7b}$$

yielding

$$\alpha^{2P} = 216 \text{ a.u.} , \tag{5.7c}$$

in agreement with earlier calculations.[27] $F_1'^{\pm}$ calculated in Sec. IV are related to $F_1^{(2S)}$ and $F_1^{(2P)}$ by

$$F_1'^{\pm} = \frac{1}{(2)^{1/2}}(F_1^{(2S)} \pm F_1^{(2P)}) . \tag{5.8}$$

VI. ARBITRARY HYDROGENIC BOUND STATE IN A LARGE-ORDER MULTIPOLE FIELD

In this section we consider an arbitrary hydrogenic bound state (n,λ) with principal quantum member n, angular momentum quantum number λ, and azimuthal quantum number $m=0$ in the presence of a large-order multipole field

$$V_1 = r^L P_l , \tag{6.1a}$$

where by large order we mean $L \geq l \geq n+\lambda$ so that the interaction V_1 in Eq. (6.1a) neither causes a first-order energy shift nor a mixing among degenerate states. The cases considered earlier in Secs. II and III for a hydrogenic $2S$ state in a quadrupole or higher multipole field and that for the hydrogenic $2P$ state in an octupole or higher multipole field both fall into the general category considered in this section.

For an arbitrary hydrogenic bound state (n,λ), we have

$$G^{n\lambda} = r/n , \tag{6.1b}$$

and

$$F_0^{n\lambda} = N(n,\lambda)\left[\frac{2r}{n}\right]^\lambda \eta(-(n-\lambda-1), 2\lambda+2, 2r/n) , \tag{6.2}$$

where

$$N(n,\lambda) \equiv \frac{1}{(2\lambda+1)!}\left[\frac{(n+\lambda)!}{(n-\lambda-1)!2n}\right]^{1/2}\left[\frac{2}{n}\right]^{3/2} \tag{6.3}$$

in a normalization factor for the state (n,λ), and $\eta(\alpha,\beta,x)$ is the confluent hypergeometric function. Since we restrict ourselves to $l \geq n+\lambda$, there will be no first-order energy shift. Using Eqs. (6.1b) and (6.2), we find

$$2\vec{\nabla} F_0^{n\lambda}\cdot\vec{\nabla} G^{n\lambda} - \nabla^2 F_0^{n\lambda} = \frac{2}{n}\frac{1}{r}(n-1)F_0^{n\lambda} \tag{6.4}$$

and so we can divide $F_0^{n\lambda}$ from both sides of Eq. (1.18). Henceforth, we drop the superscript $n\lambda$. The right-hand side (rhs) of Eq. (1.18) then becomes

$$2F_0V_1=2\left[\frac{2}{n}\right]^{\lambda}N(n,\lambda)\sum_{k=0}^{n-\lambda-1}\frac{(\lambda+1-n)_k}{(2\lambda+2)_k}\left[\frac{2}{n}\right]^{k}r^{L+\lambda+k}\sum_{j}\alpha_j(l,\lambda)Y_j^0\,, \tag{6.5}$$

where Pochhammer's symbol $(a)_k$ is defined as

$$(a)_k\equiv\Gamma(a+k+1)/\Gamma(a+1) \tag{6.6}$$

and

$$\alpha_j(l,\lambda)\equiv\sqrt{(2\lambda+1)(2j+1)}\begin{bmatrix} l & \lambda & j\\ 0 & 0 & 0\end{bmatrix}^2 \tag{6.7}$$

is the usual coupling coefficient between Y_λ^0 and P_l and

$$\begin{bmatrix} l & \lambda & j\\ 0 & 0 & 0\end{bmatrix}$$

is the usual 3-j symbol. We seek the solution for F_1 in the form

$$F_1=N(n,\lambda)\sum_{j}R_j(r)\alpha_j(l,\lambda)Y_j^0\,. \tag{6.8}$$

Then Eq. (1.18) becomes

$$r\frac{\partial^2}{\partial r^2}(rR_j)-j(j+1)R_j-\frac{2r^2}{n}\frac{\partial}{\partial r}R_j+\frac{2(n-1)}{n}rR_j=2\left[\frac{2}{n}\right]^{\lambda}\sum_{k=0}^{n-\lambda-1}\frac{(\lambda+1-n)_k}{(2\lambda+2)_k}\left[\frac{2}{n}\right]^{k}r^{L+\lambda+k+2}\,. \tag{6.9}$$

To solve Eq. (6.9), we expand $R_j(r)$ in power series:

$$R_j(r)=\sum_{\mu}a_\mu^j r^\mu\,. \tag{6.10}$$

Then Eq. (6.9) is transformed to the following indicial equation:

$$(\mu+j+1)(\mu-j)a_\mu^j-\frac{2}{n}(\mu-n)a_{\mu-1}^j=2\left[\frac{2}{n}\right]^{\lambda}\sum_{k=0}^{n-\lambda-1}\frac{(\lambda+1-n)_k}{(2\lambda+2)_k}\left[\frac{2}{n}\right]^{k}\delta_{\mu,L+\lambda+k+2}\,. \tag{6.11}$$

The marvelous thing about Eq. (6.11) is the fact that it is linear so that the solution to a_μ^j can be sought in the form

$$a_\mu^j\equiv\sum_{k=0}^{n-\lambda-1}\left[\frac{2}{n}\right]^{\lambda+k}\frac{(\lambda+1-n)_k}{(2\lambda+2)_k}a_{\mu,k}^j\,. \tag{6.12}$$

Putting Eq. (6.12) into (6.11), we find

$$(\mu+j+1)(\mu-j)a_{\mu,k}^j-\frac{2}{n}(\mu-n)a_{\mu-1,k}^j=2\delta_{\mu,L+\lambda+k+2} \tag{6.13}$$

which is an indicial equation whose form we have encountered in Secs. II and III. The solution to $a_{\mu k}^j$ in Eq. (6.13) can be written in a compact form, after incorporating the fact that $l\geq n+\lambda$ and $n\geq\lambda+1$:

$$a_{\mu,k}^j=\begin{cases}\dfrac{-2(\mu-n)!(\frac{1}{2}n)^{\mu_{\max,k}-\mu+1}}{(\mu+j+1)!(\mu-j)!}\dfrac{(\mu_{\max,k}+1+j)!(\mu_{\max,k}-j)!}{(\mu_{\max,k}-n+1)!} & \text{for } j\leq\mu\leq\mu_{\max,k}\\ 0 \text{ otherwise}\,, & \end{cases} \tag{6.14}$$

where

$$\mu_{\max,k}\equiv L+\lambda+1+k\,. \tag{6.15}$$

Putting Eqs. (6.8), (6.10), (6.12), and (6.14) together, we get the first-order correction F_1:

$$F_1=N(r,\lambda)\sum_{j=l-\lambda}^{l+\lambda}\alpha_j(l,\lambda)Y_j^0\sum_{k=0}^{n-\lambda-1}\left[\frac{2}{n}\right]^{\lambda+k}\frac{(\lambda+1-n)_k}{(2\lambda+2)_k}\sum_{\mu=j}^{L+\lambda+1+k}a_{\mu,k}^j r^u\,. \tag{6.16}$$

Knowing F_1, we can calculate the following sum rule:

$$S^{n\lambda}_{Ll} \equiv \sum_{m} \frac{|\langle n,\lambda | r^L P_l | m \rangle|^2}{E_n - E_m} , \quad L \geq l \geq n+\lambda . \tag{6.17}$$

In terms of F_0, F_1, and G, the sum rule can be written as

$$S^{n\lambda}_{Ll} = \int F_0 F_1 r^L P_l e^{-2G} d^3 r \tag{6.18}$$

which can be put in the final form

$$S^{n\lambda}_{Ll} = \sum_{j,\nu,k,\mu} \frac{(\lambda+1-n)_\nu}{(2\lambda+2)_\nu} \frac{(\lambda+1-n)_k}{(2\lambda+2)_k} \left[\frac{n}{2} \right]^{\mu+L+3-\lambda-k} a^{j}_{\mu,k} \times [\alpha_j(l,\lambda) N(n,\lambda)]^2 (\mu+\nu+\lambda+L+2)! , \tag{6.19}$$

where the summation ranges for j, k, and μ are the same as those in Eq. (6.16) and the summation range for ν is the same as that in k. The 2^L polarizability for the $n\lambda$ state where $L \geq n+\lambda$ is given by $-2S^{n\lambda}_{LL}$.

VII. SUMMARY REMARKS

In this paper we have suggested a modification of the usual Rayleigh-Schrödinger perturbation theory for the bound states of a multidimensional single-particle system. This consists of a perturbation expansion on the nodal part of the wave function, leaving the gradient of the logarithm of the wave-function envelope intact as the perturbation is turned on. It is suggested that adjustment to the wave-function envelope be made after the perturbation calculation has been completed up to a desired order. The adjustment is based on the expected relation between the logarithm of the asymptotic form of the wave function and the energy. The nodal part of the wave function can then be adjusted accordingly after expansion of the envelope part in power series in the coupling constant. The same method can be extended to degenerate perturbation theory. But it requires additional bookkeeping of indices. Moreover, the ith-order correction to the wave function is determined by the $(i+1)$th-order equation if the degeneracy is lifted in first order, as is the case in ordinary degenerate perturbation theory.

We then used this modified perturbation method to calculate the changes in the wave functions and energies of the hydrogenic $2S$ and $2P_0$ states in a multipole field, and hence the static multipole polarizabilities in closed forms. For multipoles higher than the dipole, there is no degenerate mixing between the $2S$ and $2P_0$ states. However, in the presence of the dipole field the degenerate method must be used. We have used the degenerate method to calculate the corrections to the wave functions to second order in spherical coordinates and the energies to fourth order. We have also calculated the first-order corrections to the wave functions of the pure $2S$ and $2P_0$ hydrogenic states in a dipole field exclusive of the degenerate contributions and hence the dipole polarizabilities of the states. We also showed that for an arbitrary bound hydrogenic state in a large-order multipole, the first-order correction to the wave function and hence the polarizabilities can be calculated in closed forms. Finally, in the Appendix we show how the second-order energy shift of an atom in a rotationally invariant state in an external electrical potential is related to the multipole polarizability given in sum-rule form by Dalgarno.

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APPENDIX: SECOND-ORDER ENERGY SHIFT OF AN ATOM IN A ROTATIONALLY INVARIANT STATE IN AN EXTERNAL ELECTRICAL POTENTIAL

The energy of an atom in an external electrical potential ϕ is

$$\Delta E = \int \rho(\vec{r}) \Phi(\vec{r}) d\vec{r} , \tag{A1}$$

which, on a Taylor expansion, becomes

$$\Delta E = \sum_{L=0}^{\infty} \Delta E_L , \tag{A2}$$

where

$$\Delta E_L = \frac{1}{L!} \int \rho(\vec{r}) x_{i_1} \cdots x_{i_L} \partial_{i_1} \cdots \partial_{i_L} \Phi(0) d^3 r . \tag{A3}$$

Here ρ is the total charge density

$$\rho(\vec{r}) = \rho_e(\vec{r}) + \rho_N(\vec{r}) , \tag{A4}$$

where

$$\rho_e(\vec{r}) = \psi^* \psi , \tag{A5}$$

the square of the electronic wave function, is the electronic charge density and

$$\rho_N(\vec{r}) = -\delta(\vec{r}) \tag{A6}$$

is the nuclear charge density and the electronic and nuclear charges are normalized to ±1. Charge neutrality of the atom implies $E_0 = 0$ to all orders in perturbation theory, the perturbation parameter being the external potential Φ. ρ_N contributes to E_0 only.

For an atom in a rotationally invariant state ϕ, to the lowest (first) order in Φ,

$$\int \rho(\vec{r}) x_{i_1} \cdots x_{i_L} \partial_{i_1} \cdots \partial_{i_L} \Phi(0) d^3 r = 0 \,, \quad L \neq 0 \tag{A7}$$

for any of the following reasons: (i) parity considerations when L is odd, or (ii) angular momentum addition triangle rule when L is even, or (iii) when L is even, contraction of indices leading to $\nabla^2 \Phi = 0$ since Φ is an external potential.

Thus the lowest-order energy shift induced by the external potential is second order in Φ when the electronic change density is polarized by the external field. Proceeding in the usual fashion in perturbation theory, one obtains the energy shift

$$\Delta E_{(2)} = \sum T_{i_1,\ldots,i_L}^{j_1,\ldots,j_N} \Phi_{j_1,\ldots,j_N}^{i_1,\ldots,i_L} / (L!N!) \,, \tag{A8}$$

where

$$T_{i_1,\ldots,i_L}^{j_1,\ldots,j_N} = \sum_n \frac{\langle \phi | x_{i_1} \cdots x_{i_L} | n \rangle \langle n | x_{j_1} \cdots x_{j_N} | \phi \rangle}{E_\phi - E_n} \,, \tag{A9}$$

and

$$\Phi_{i_1,\ldots,i_N}^{j_1,\ldots,j_L} = [\partial_{1_1} \cdots \partial_{i_L} \Phi(0)][\partial_{j_1} \cdots \partial_{j_N} \Phi(0)] \,, \tag{A10}$$

and repeated indices are summed over in Eq. (A8). Because of parity, N and L must be either both odd or both even. Furthermore, because of rotational invariance, the tensor T must be proportional to tensors constructed out of $\delta_{i_b}^{j_a}$, $\delta^{j_a j_b}$, or $\delta_{i_a i_b}$. However, the latter two types of tensors would contract to $\nabla^2 \Phi$ which equals zero since Φ is an external potential. Thus, the only nonzero contribution in Eq. (A8) comes from $L = N$. Hence

$$\Delta E_{(2)} = \sum_L T_{i_1,\ldots,i_L}^{j_1,\ldots,j_L} \Phi_{j_1,\ldots,j_L}^{i_1,\ldots,i_L} / (L!)^2 \,. \tag{A11}$$

Again, rotational invariance arguments lead to

$$\begin{aligned} T_{i_1,\ldots,i_L}^{j_1,\ldots,j_L} = {} & B(L) \sum_{\sigma \epsilon S_L} \delta_{j_1 i_{\sigma(1)}} \delta_{j_2 i_{\sigma(2)}} \cdots \delta_{j_L i_{\sigma(L)}} + C(L) \sum_{\sigma \epsilon S_L} \sum_{a \neq b} \delta^{j_a j_b} \delta_{i_a i_b} \prod_{k,m \neq a,b} \delta_{j_k i_{\sigma(m)}} \\ & + D(L) \sum_{\sigma \epsilon S_L} \sum_{a \neq b \neq c \neq d} \delta^{j_a j_b} \delta_{i_a i_b} \delta^{j_c j_d} \delta_{i_c i_d} \prod_{k,m \neq a,b,c,d} \delta_{j_k i_{\sigma(m)}} + \cdots \,, \end{aligned} \tag{A12}$$

where S_L denotes the set of all permutations of $\{1,\ldots,L\}$. The only terms on the rhs of Eq. (A12) that would give nonzero contribution to the sum in Eq. (A11) are the first type of tensors multiplying $B(L)$ since the others lead to $\nabla^2 \Phi$ which equal zero. Since there are $L!$ possible tensors arising from the $L!\sigma$ permutations and the tensor Φ is symmetric with respect to its upper set or lower set indices, we finally have

$$\Delta E_{(2)} = \sum_L B(L) \Phi_{i_1,\ldots,i_L}^{i_1,\ldots,i_L} / L! \tag{A13}$$

The remaining task is to identify $B(L)$ with the static 2^L-order multipole polarizability given by Dalgarno in Eq. (3.1). Now consider the sum rule

$$S^\phi(L) \equiv \sum_n \frac{\langle \phi | (x_-)^L | n \rangle \langle n | (x_+)^L | n \rangle}{E_0^{(\phi)} - E_0^{(n)}} \,, \tag{A14}$$

where

$$x_\pm = \frac{x \pm iy}{(2)^{1/2}} = r Y_1^{\pm 1} \left[\frac{4\pi}{3} \right]^{1/2} . \tag{A15}$$

According to the arguments leading to Eq. (A12),

$$S^\phi(L) = B(L) L! \tag{A16}$$

since in this particular sum rule there is no possible contraction among the upper set or among the lower set of indices to form nonzero Kronecker deltas. Thus one establishes

$$B(L) = \frac{1}{L!} \sum_n \frac{\langle \phi | x_-^L | n \rangle \langle n | x_+^L | \phi \rangle}{E_0^{(\phi)} - E_0^{(n)}} \,. \tag{A17}$$

Next, one can prove either by direct combination of spherical harmonics or by mathematical induction that

$$(x_\pm)^L = r L Y_L^{\pm L} \frac{L!L!2^L(4\pi)}{(2L+1)!} \,. \tag{A18}$$

Hence,

$$B(L) = \frac{L!2^L 4\pi}{(2L+1)!} \sum_n \frac{\langle \phi | r^L Y_L^{-L} | n \rangle \langle n | r^L Y_L^L | \phi \rangle}{E_0^{(\phi)} - E_0^{(n)}} \,, \tag{A19}$$

$$= \frac{L!2^L 4\pi}{(2L+1)!} \sum_n \frac{\langle \phi | r^L Y_L^0 | n \rangle \langle n | r^L Y_L^0 | \phi \rangle}{E_0^{(\phi)} - E_0^{(n)}} \,. \tag{A20}$$

The second relation follows from rotational invariance. On using the relation between spherical harmonics and Legendre polynomials and the Dalgarno[22] form of 2^L multipole polarizability, one has

$$B(L) = -\frac{L!2^L}{2(2L)!} \alpha_{2^L} \,. \tag{A21}$$

Using this in Eq. (A13), one obtains Eq. (2.12).[28,29]

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