Hydrogen atom in a static multipole field

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It is shown that the method of logarithmic perturbation expansion can be used to obtain the corrections to the energy and the logarithm of the wave function of the ground state of a hydrogen atom in a static multipole field, or a linear combination of static multipole fields to any order in perturbation theory.

The problem of an atom in a static multipole field is often encountered in both atomic and solid state physics. The simplest of such problems, that of the Stark effect in the hydrogen atom, has recently been investigated in detail to arbitrarily higher-order corrections in perturbation theory.[1] In parabolic coordinates, this problem is still separable, and reduces to an "eigenvalue" problem of the separation constants.[2] A number of authors[3] have recently shown that by considering the logarithmic derivative of the wave function instead of the wave function itself, the separated equations in parabolic coordinates are reducible to the Ricatti form. This reducibility can be extended to all eigenvalue problems of the Sturm-Liouville type. The perturbative solution to the one-dimensional wave equation in the Ricatti form has been discussed by Price,[4] Polikanov,[5] the present authors,[6] and Turbiner.[7] We have recently given the name "logarithmic perturbation expansion" to this perturbative approach to the eigenvalue problem and have extended this technique to nonrelativistic problems in three dimensions.[8]

In this paper, we would like to show that the technique of logarithmic perturbation expansion can be applied to the problem of the ground state of the hydrogen atom in a static multipole field to obtain the corrections to the energy and the logarithm of the wave function to all orders in perturbation theory. We shall show that to each order, the correction to the logarithm of the wave function is obtainable as the solution to a second-order differential equation, for which a closed form exists and that the correction to the energy is obtainable from the lower-order corrections to the logarithm of the wave function with suitable vector coupling coefficients. Since there exists a one-to-one correspondence between a wave function and its logarithm, the existence of a closed-form solution to the correction of the logarithm of the wave function to each order im-

plies the existence of a closed-form solution to the correction to the wave function to each order.

To make this paper self-contained, we give here a concise discussion of our technique of logarithmic perturbation expansion. Let $\psi_0(x)$, E_0, $\psi(x)$, and E denote the eigenstates and eigenenergies of the unperturbed Hamiltonian H_0 and the total Hamiltonian H, respectively, where $H = H_0 + \alpha V_1$, V_1 being the perturbation. We next define

$$\psi(x) \equiv \exp[-G(x)] \tag{1}$$

and

$$\vec{g}(x) = \vec{\nabla} G(x). \tag{2}$$

We shall set $m = \hbar = a_0 = 1$, where a_0 is the Bohr radius. Then the Schrödinger equation becomes

$$\operatorname{div} \vec{g} - \vec{g}^2 = 2(E - V_0 - \alpha V_1). \tag{3}$$

On expanding G, $\vec{g}$, and E as power series in α,

$$G = G_0 + \alpha G_1 + \alpha^2 G_2 + \cdots, \tag{4}$$

$$\vec{g} = \vec{g}_0 + \alpha \vec{g}_1 + \alpha^2 \vec{g}_2 + \cdots, \tag{5}$$

$$E = E_0 + \alpha E_1 + \alpha^2 E_2 + \cdots, \tag{6}$$

and comparing coefficients of the various powers of α in Eq. (3), we arrive at the following hierarchy of equations:

$$\operatorname{div} \vec{g}_0 - \vec{g}_0^2 = 2(E_0 - V_0), \tag{7}$$

$$\operatorname{div} \vec{g}_1 - 2\vec{g}_0 \cdot \vec{g}_1 = 2(E_1 - V_1), \tag{8}$$

and

$$\operatorname{div} \vec{g}_i - 2\vec{g}_0 \cdot \vec{g}_i = 2\left(E_i + \frac{1}{2} \sum_{j=1}^{i-1} \vec{g}_j \cdot \vec{g}_{i-j}\right) \tag{9}$$

for $i \geq 2$. The factor $-\frac{1}{2}\sum_{j=1}^{i-1} \vec{g}_j \cdot \vec{g}_{i-j}$ in Eq. (9) can be looked upon as the "effective" ith-order perturbation potential and hence Eq. (9) is similar in form to Eq. (8), which gives the first-order corrections. The square of the unperturbed wave function

$$\rho(x) \equiv \psi_0^2(x) = e^{-2G_0} \tag{10}$$

serves as an integrating factor in Eqs. (8) and (9):

$$\text{div}(\vec{g}_i e^{-2G_0}) = 2(E_i - V_i)e^{-2G_0} . \tag{11}$$

On integrating this over all space, and using Green's theorem and the fact that ψ_0 vanishes at infinity and is normalized, we obtain

$$E_i = \int V_i \rho , \tag{12}$$

where

$$V_i = -\frac{1}{2} \sum_{j=1}^{i-1} \vec{g}_j \cdot \vec{g}_{i-j}, \quad \text{for } i \neq 1 . \tag{13}$$

Since V_1 and G_0, and hence $\vec{g}_0$ and ρ are known, Eq. (8) reduces to a linear second-order inhomogeneous vector differential equation for the function G_1. After G_1 is solved, $\vec{g}_1$ is known and Eq. (9) can be solved for $i = 2$ in the same spirit as in Eq. (8), and so on up the hierarchy.

In this paper, we wish to show that, for a hydrogen atom whose unperturbed state is the ground state, when V_1 has the form

$$V_1 = \sum_{L \geq l \geq 0} Q_{Ll} r^L \mathcal{Y}_{l0} , \tag{14}$$

the hierarchy of equations can be solved for all i. Since Eqs. (8) and (9) are linear it is sufficient to consider a perturbation just of the form

$$V_1 = Q_{Ll} r^L \mathcal{Y}_{l0}, \quad L \geq l . \tag{15}$$

The first-order energy shift corresponding to this perturbation potential is easily obtained as

$$E_1 = \frac{Q_{Ll}}{(4\pi)^{1/2}} \frac{(L+1)!}{2^{L+1}} \delta_{l0} . \tag{16}$$

For a hydrogen atom whose unperturbed state is the ground state

$$G_0 = r + \text{const} \tag{17}$$

and so

$$\vec{g}_0 = \vec{\nabla} G_0 = \hat{r} , \tag{18}$$

and Eqs. (8) and (9) reduce to

$$\nabla^2 G_i - 2 \frac{\partial}{\partial r} G_i = 2(E_i - V_i), \quad i \geq 1 . \tag{19}$$

Equation (19) indicates that G_i is indeterminate up to an additive constant. This additive constant to the logarithm of the wave function is a multiplicative constant to the wave function, and hence can be fixed by normalization. We shall therefore ignore any additive constant in the solution of G_i but require the wave function be normalized. Since

$$\nabla^2 G = \frac{1}{r} \frac{\partial^2}{\partial r^2} (rG) - \frac{\vec{L}^2}{r^2} G , \tag{20}$$

where $\vec{L}$ is the orbital-angular-momentum vector operator, for a perturbation potential V_1 as given in Eq. (15) we seek a solution of G_1 in the form

$$G_1^{Ll}(\vec{r}) = [R_{Ll}(r)/r]\mathcal{Y}_{l0} \equiv \mathcal{G}_{Ll}^{(r)} \mathcal{Y}_{l0} . \tag{21}$$

We shall later show that all higher-order effective perturbation potentials as given by Eq. (13) can be cast into the form in Eq. (14). The linearity of the differential Eq. (19) thus implies that the solution to G_i can be sought in a manner similar to that of G_1. Putting Eqs. (21) and (15) into Eq. (19) and making use of Eq. (20), we arrive at the following differential equation for R_{Ll}:

$$R_{Ll}'' - 2R_{Ll}' - \left(\frac{l(l+1)}{r} - \frac{2}{r}\right)R_{Ll}$$
$$+ 2Q_{Ll}\left(r^{L+1} - \frac{r(L+2)!}{2^{L+1}} \delta_{l0}\right) = 0 . \tag{22}$$

We seek the solution in the form

$$R_{Ll} = \sum_n a_n^{Ll} r^n . \tag{23}$$

Equation (22) then reduces to the following indicial equation:

$$[(n+2)(n+1) - l(l+1)] a_{n+2}^{Ll} - 2n a_{n+1}^{Ll}$$
$$+ 2Q_{Ll}\{\delta_{n,L+1} - [(L+2)!/2^{L+1}] \delta_{n1}\delta_{l0}\} = 0 . \tag{24}$$

The normalizable solution can be obtained as

$$a_n^{Ll} = \begin{cases} Q_{Ll} \dfrac{(L-l+1)!(L+l+2)!}{2^{L+2}(L+1)!} \dfrac{(n-2)!2^n}{(n+l)!(n-l-1)!} \\ \qquad\qquad (L+2 \geq n \geq l+1+2\delta_{l0}) \\ 0, \quad \text{otherwise.} \end{cases} \tag{25}$$

It may be noted that when $l = 0$, a_1^{L0} is arbitrary. But since $a_1^{L0} \mathcal{Y}_{00}$ that enters G_1 is an additive constant, a_1^{L0} can be absorbed into the undetermined constant mentioned earlier in the solution of G_1, which can be fixed by normalization. It is then straightforward to show that $\vec{g}_1^{Ll} \cdot \vec{g}_1^{L'l'} \equiv \vec{\nabla} G_1^{Ll} \cdot \vec{\nabla} G_1^{L'l'}$ can be written as

$$\vec{g}_1^{Ll} \cdot \vec{g}_1^{L'l'} = \sum_{\lambda, \Lambda} [1 + (-1)^{l+l'+\lambda}]$$
$$\times Q_{\Lambda, \lambda}^l(L, l, L', l') r^\Lambda \mathcal{Y}_{\lambda 0} , \tag{26}$$

where the summation limit for λ is from 0 to $l + l'$ and that of Λ is from $(l + l' + 2\delta_{l0} + 2\delta_{l'0} - 2)$ to $L + L'$,

$$Q_{\Lambda\lambda}^{I}(L,l,L',l') = \sum_{\substack{n=l+2\delta_{l0} \\ }}^{\Lambda+2-l'-2\delta_{l'0}} \tfrac{1}{2} T_n(L,l,L',l',\lambda,\Lambda)\, a_{n+1}^{Ll}\, a_{\Lambda-n+3}^{L'l'}, \tag{27}$$

$$
\begin{aligned}
T_n(L,l,L',l',\lambda,\Lambda) =\ & (n-l)(\Lambda-n-l'+2)[\alpha_l\alpha_{l'}\,V(l+1,l'+1,\lambda;0,0)-\mathcal{C}_l\,\mathcal{C}_{l'}\,V(l+1,l'+1,\lambda;1,-1)] \\
& + (n+l+1)(\Lambda-n+l'+3)[\mathfrak{B}_l\mathfrak{B}_{l'}\,V(l-1,l'-1,\lambda;0,0)-\mathfrak{D}_l\,\mathfrak{D}_{l'}\,V(l-1,l'-1,\lambda;1,-1)] \\
& + (n-l')(\Lambda-n+l+3)[\alpha_l\mathfrak{B}_{l'}\,V(l+1,l'-1,\lambda;0,0)-\mathcal{C}_l\mathfrak{D}_{l'}\,V(l+1,l'-1,\lambda;1-1)] \\
& + (n-l')(\Lambda-n+l+3)[\alpha_{l'}\mathfrak{B}_l\,V(l'+1,l-1,\lambda;0,0)-\mathcal{C}_{l'}\mathfrak{D}_l\,V(l'+1,l-1,\lambda;1,-1)], \tag{28}
\end{aligned}
$$

$$\alpha_l \equiv \frac{l+1}{[(2l+3)(2l+1)]^{1/2}}, \tag{29}$$

$$\mathfrak{B}_l \equiv \frac{l}{[(2l+1)(2l-1)]^{1/2}}, \tag{30}$$

$$\mathcal{C}_l \equiv \left(\frac{(l+2)(l+1)}{(2l+3)(2l+1)}\right)^{1/2}, \tag{31}$$

$$\mathfrak{D}_l \equiv \left(\frac{l(l-1)}{(2l+1)(1l-1)}\right)^{1/2}, \tag{32}$$

and where

$$V(l,l',\lambda;m,m') \equiv \int \mathcal{Y}_{lm}\mathcal{Y}_{l'm'}\mathcal{Y}_{\lambda(m+m')} \tag{33}$$

is the vector coupling coefficient.

By now, we have all the results necessary to obtain the perturbative solution to the problem of the ground state of hydrogen in a linear combination of static multipole fields. The "effective" potential V_2 is a linear combination of the type of the potential V_1 which we consider in Eq. (15). In particular, only the $\lambda=0$ term in the sum in Eq. (26) will contribute to the next-order energy shift. For example, when $V_1 = Q_{Ll}r^L\mathcal{Y}_{l0}$, the second-order energy shift is given by

$$E_2 = \frac{-1}{(4\pi)^{1/2}} \sum_{\Lambda} Q_{\Lambda 0}^{I}(L,l,L,l)\,\frac{(\Lambda+2)!}{2^{\Lambda+1}} \tag{34}$$

and the "effective" second-order perturbation potential is given by

$$V_2 = -\sum_{\Lambda\lambda} Q_{\Lambda\lambda}^{I}(L,l,L,l)\,r^{\Lambda}\mathcal{Y}_{\lambda,0}. \tag{35}$$

Because of the linearity of the differential Eq. (9), G_2 can be solved in the same fashion as G_1.

We write

$$G_2 = \sum_{\Lambda\lambda} \mathcal{G}_{\Lambda\lambda}^{I}\mathcal{Y}_{\lambda 0}, \tag{36}$$

$$\mathcal{G}_{\Lambda\lambda}^{I} = R_{\Lambda\lambda}^{I}/r, \tag{37}$$

$$R_{\Lambda\lambda}^{I} = \sum_n a_n^{I,\Lambda\lambda} r^n. \tag{38}$$

Then the set of coefficients $a_n^{I,\Lambda\lambda}$ is given by Eq. (25) except Q_{Ll} has to be replaced by $Q_{\Lambda l}^{I}$. With G_2 thus obtained, one can get $\vec{g}_2\cdot\vec{g}_1$ and hence V_3 which is again a linear combination of the type of potential we have considered in V_1, and we can write

$$V_3 = \sum_{\Lambda\lambda} Q_{\Lambda\lambda}^{II} r^{\Lambda}\mathcal{Y}_{\lambda,0}, \tag{39}$$

and G_3 can be obtained in the same manner as G_2. The third-order energy shift E_3 is given by

$$E_3 = \frac{-1}{\sqrt{4\pi}} \sum_{\Lambda} Q_{\Lambda 0}^{II}\,\frac{(\Lambda+2)!}{2^{\Lambda+1}}. \tag{40}$$

Obviously, this process can be continued to obtain G_i and E_i to all orders.

Lastly, for $L=l$ in V_1, our results for the second-order energy shift are in agreement with those of Dalgarno and Lewis,[9] Bell,[10] and the static limit of the dynamic multipole polarizability.[11]

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