Third-order Stark effect: An operator approach*

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The third-order Stark effect is re-examined using an operator method presented by Schwinger. By observing an identity for the perturbed part of the Hamiltonian and by using commutation relations, we are able to obtain the energy spectra of hydrogenic atoms in a constant electric field without solving the Schrödinger equation. Our result confirms that of Doi and El-Sherbini.

I. INTRODUCTION

The influence of an external electric field on atomic spectra was discovered by Stark in 1913 and is known as the Stark effect. The theoretical calculations of this effect were carried out almost half a century ago, by solving the Schrödinger equation for the hydrogenic atom using the method of separation of variables in parabolic coordinates.[1] However, this method becomes quite involved when one tries to calculate higher-order perturbations to the energy spectra.[1,2]

A much simpler method, developed particularly for this problem, was presented some years ago by Schwinger[3] and was used to recalculate the first- and second-order Stark effects. By making use of the commutation relations among the generators of the symmetry group of the hydrogenic atom and by observing an identity for the perturbed part of the Hamiltonian [Eq. (37)], he was able to obtain the energy spectra of the system without solving the Schrödinger equation. The purpose of this paper is to first review Schwinger's method, which is nowhere available, and then apply it (with slight modification) to calculate the third-order Stark effect. Hopefully, this technique can be used to solve some other problems in atomic and molecular physics.

II. UNPERTURBED HYDROGENIC ATOMS

The Hamiltonian for the hydrogenic atom is

$$H_0=\vec{p}^2/2\mu - Ze^2/r\,, \tag{1}$$

where μ is the reduced mass, r is the relative distance, and $\vec{p}$ is the relative momentum. It is well known that there are two constant operators in this system: The orbital angular momentum

$$\hbar\vec{L}=\vec{r}\times\vec{p}\,, \tag{2}$$

and the axial vector

$$\vec{A}=\vec{r}/r-(\hbar/\mu Ze^2)\tfrac{1}{2}(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})\,. \tag{3}$$

They obey the commutation relations

$$[L_i\,,L_j]=i\epsilon_{ijk}L_k\,, \tag{4}$$

$$[L_i\,,A_j]=i\epsilon_{ijk}A_k\,, \tag{5}$$

$$[A_i\,,A_j]=i\epsilon_{ijk}(-2\hbar^2H_0/\mu Z^2e^4)L_k\,. \tag{6}$$

Some of their properties are

$$\vec{A}\cdot\vec{L}=0,\quad \vec{r}\cdot\vec{L}=0\,, \tag{7}$$

$$\vec{A}^2=1+(2\hbar^2H_0/\mu Z^2e^4)(\vec{L}^2+1)\,. \tag{8}$$

The angular momenta[4]

$$\vec{J}^{(1)}=\tfrac{1}{2}[\vec{L}+(-\mu Z^2e^4/2\hbar^2H_0)^{1/2}\vec{A}]\,, \tag{9}$$

$$\vec{J}^{(2)}=\tfrac{1}{2}[\vec{L}-(-\mu Z^2e^4/2\hbar^2H_0)^{1/2}\vec{A}]\,, \tag{10}$$

obey the commutation relations

$$[J_i^{(a)},J_j^{(a)}]=i\epsilon_{ijk}J_k^{(a)},\quad a=1 \text{ or } 2, \tag{11}$$

$$[J_i^{(1)},J_j^{(2)}]=0\,, \tag{12}$$

which are the algebraic statement that hydrogenic atoms possess the symmetry group $O(4)=SO(3)\times SO(3)$. One also notes that the two angular momenta have equal magnitudes since

$$(\vec{J}^{(1)})^2=(\vec{J}^{(2)})^2=\tfrac{1}{4}(-\mu Z^2e^4/2\hbar^2H_0-1)\,. \tag{13}$$

The states of the system can be completely specified by the quantum numbers j, m_1, and m_2, which are eigenvalues of the operators $(\vec{J}^{(a)})^2$, $J_z^{(1)}$, and $J_z^{(2)}$, respectively. That is, if $|jm_1m_2\rangle$ is the eigenstate, then we have

$$(\vec{J}^{(1)})^2|jm_1m_2\rangle=(\vec{J}^{(2)})^2|jm_1m_2\rangle=j(j+1)|jm_1m_2\rangle\,, \tag{14}$$

$$J_z^{(a)}|jm_1m_2\rangle=m_a|jm_1m_2\rangle\,,\quad a=1 \text{ or } 2\,, \tag{15}$$

where

$$j=0,\tfrac{1}{2},1,\tfrac{3}{2},\ldots,\quad m_a=-j,-j+1,\ldots,j-1,j\,. \tag{16}$$

Another set of quantum numbers which are conventionally used to solve the hydrogenic-atom problem are

$$n=2j+1, \quad k_a=\tfrac{1}{2}(n-1)-m_a, \quad a=1 \text{ or } 2, \tag{17}$$

with

$$n=1,2,3,\ldots \quad \text{and} \quad k_a=0,1,2,\ldots,n-1. \tag{18}$$

Now Eqs. (13) and (14) imply

$$4j(j+1)=-\mu Z^2e^4/2\hbar^2E_n-1$$

or

$$E_n=-\mu Z^2e^4/2n^2\hbar^2. \tag{19}$$

This is the well-known Bohr formula for the energy levels of the hydrogenic atom. The eigenvalues of L_z and A_z are

$$L_z'=(J_z^{(1)}+J_z^{(2)})'=m_1+m_2\equiv m, \tag{20}$$

$$nA_z'=(J_z^{(1)}-J_z^{(2)})'=m_1-m_2=-(k_1-k_2)\equiv -k. \tag{21}$$

We note that the bases $|jm_1m_2\rangle$ or $|nk_1k_2\rangle$ are not eigenstates of the operators $\vec{L}^2$ and $i(\vec{A}\times\vec{L}_z)$. However, their expectation values can be easily evaluated as

$$\langle\vec{L}^2\rangle=\tfrac{1}{2}(n^2+m^2-k^2-1), \tag{22}$$

$$i\langle(\vec{A}\times\vec{L})_z\rangle=k/n. \tag{23}$$

III. SCHWINGER'S APPROACH

In this section, we will review Schwinger's method of calculating the first- and second-order Stark effects.[3] In a constant electric field $\vec{\mathcal{E}}$, the Hamiltonian of the system becomes

$$H=H_0+H_1, \tag{24}$$

where

$$H_1=-e\vec{\mathcal{E}}\cdot\vec{r}. \tag{25}$$

In the usual perturbation approach, one introduces a parameter λ and considers the new Hamiltonian

$$H_\lambda=H_0+\lambda H_1. \tag{26}$$

The corresponding Heisenberg equations of motion are

$$\mu\frac{d\vec{r}}{dt}=\frac{1}{i\hbar}[\vec{r},\mu H_\lambda]=\vec{p}, \tag{27}$$

$$\frac{d\vec{p}}{dt}=\frac{1}{i\hbar}[\vec{p},H_\lambda]=-\frac{Ze^2}{r^3}\vec{r}+\lambda e\vec{\mathcal{E}}. \tag{28}$$

Now if $\langle\xi_\lambda|$ is an eigenstate of H_λ with energy eigenvalue E_λ', then we have

$$\delta_{\xi_\lambda'\xi_\lambda''}E_\lambda'=\langle\xi_\lambda'|H_\lambda|\xi_\lambda''\rangle, \tag{29}$$

which, by differentiating with respect to λ, implies

$$\delta_{\xi_\lambda'\xi_\lambda''}\frac{\partial E_\lambda'}{\partial\lambda}=\langle\xi_\lambda'|\frac{\partial H_\lambda}{\partial\lambda}+\frac{i}{\hbar}[G,H_\lambda]|\xi_\lambda''\rangle, \tag{30}$$

where G is the generator of the parameter λ defined as

$$\delta\langle\xi_\lambda'|=\langle\xi_\lambda'|(i/\hbar)G\delta\lambda. \tag{31}$$

Since Eq. (30) is true for arbitrary states $\langle\xi_\lambda'|$ and $|\xi_\lambda''\rangle$, we obtain the identity[4]

$$\frac{\partial H_\lambda}{\partial\lambda}=\frac{\partial E_\lambda'}{\partial\lambda}+\frac{1}{i\hbar}[G,H_\lambda]. \tag{32}$$

The perturbation theory we will use here is as follows. By expanding E_λ' in the power series of λ,

$$E_\lambda'=E_n+\lambda E^{(1)}+\lambda^2E^{(2)}+\lambda^3E^{(3)}+\cdots, \tag{33}$$

we then identify

$$E^{(n)}=\frac{1}{n!}\left(\frac{\partial^nE_\lambda'}{\partial\lambda^n}\right)_{\lambda=0} \tag{34}$$

as the nth perturbation of the energy eigenvalue. Also from Eq. (32), we have

$$\frac{\partial E_\lambda'}{\partial\lambda}=\left\langle\frac{\partial H_\lambda}{\partial\lambda}\right\rangle_\lambda, \tag{35}$$

where

$$\langle\cdots\rangle_\lambda\equiv\langle\xi_\lambda'|\cdots|\xi_\lambda'\rangle. \tag{36}$$

The basic ingredient in Schwinger's approach is to observe the following identity:

$$\frac{\partial H_\lambda}{\partial\lambda}=-e\mathcal{E}z=\frac{3}{4}\frac{Ze^2}{H_0}e\mathcal{E}A_z+\frac{d}{dt}\bar{G}+O(\lambda), \tag{37}$$

where[5]

$$\begin{aligned}\bar{G}&=(-e\mathcal{E})[\tfrac{1}{2}x_ip_zx_i-\tfrac{1}{8}(\vec{r}\cdot\vec{p})z-\tfrac{1}{8}z(\vec{p}\cdot\vec{r})+\tfrac{1}{2}i\hbar(z-\langle z\rangle)]/H_0\\&=(-e\mathcal{E})(1/H_0)[\tfrac{1}{2}x_ip_zx_i-\tfrac{1}{8}(\vec{r}\cdot\vec{p})z\\&\qquad-\tfrac{1}{8}z(\vec{p}\cdot\vec{r})-\tfrac{1}{2}i\hbar(z-\langle z\rangle)],\end{aligned} \tag{38}$$

and, without loss of generality, we have chosen $\vec{\mathcal{E}}$ to be in the z direction. The proof of this identity will be given in Appendix A. For the first-order perturbation, we have [from Eqs. (34), (35), and (37)]

$$\begin{aligned}E^{(1)}&=\left(\frac{\partial E_\lambda'}{\partial\lambda}\right)_{\lambda=0}=\left\langle\frac{\partial H_\lambda}{\partial\lambda}\right\rangle_{\lambda=0},\\&=\tfrac{3}{4}(Ze^2/E_n)e\mathcal{E}A_z',\\&=\tfrac{3}{2}(na_0/Z)ke\mathcal{E},\end{aligned} \tag{39}$$

where we have used Eqs. (19)–(21) and defined the Bohr radius to be

$$a_0=\hbar^2/\mu e^2. \tag{40}$$

For the second-order perturbation, we have

$$E^{(2)}=\frac{1}{2}\left(\frac{\partial}{\partial\lambda}\left\langle\frac{\partial H_\lambda}{\partial\lambda}\right\rangle_\lambda\right)_{\lambda=0},$$
$$=\frac{1}{2}\frac{i}{\hbar}\left\langle\left[G,\frac{\partial H_\lambda}{\partial\lambda}\right]\right\rangle_{\lambda=0},$$
$$=\frac{1}{2}\frac{i}{\hbar}\langle[G,-e\mathcal{E}z]\rangle_{\lambda=0}\ . \tag{41}$$

We see that an explicit expression of G is required. This can be achieved by comparing Eqs. (32) and (37) at $\lambda=0$; and one obtains

$$G=\tilde{G}+\delta G, \tag{42}$$

in which δG is an arbitrary function of constant operators. One notes that

$$\langle[\delta G,-e\mathcal{E}z]\rangle_{\lambda=0}=\left\langle\left[\delta G,\frac{3}{4}\frac{Ze^2}{H_0}e\mathcal{E}A_z+\frac{d\tilde{G}}{dt}\right]\right\rangle_{\lambda=0},$$
$$=\left\langle\frac{d}{dt}[\delta G,\tilde{G}]\right\rangle_{\lambda=0}=0, \tag{43}$$

and

$$(i/\hbar)\langle[\tilde{G},-e\mathcal{E}z]\rangle_{\lambda=0}=[(e\mathcal{E})^2/E_n][\tfrac{3}{4}\langle z^2\rangle_{\lambda=0}+\tfrac{1}{2}\langle r^2\rangle_{\lambda=0}-(\langle z\rangle_{\lambda=0})^2], \tag{44}$$

which then imply

$$E^{(2)}=[(e\mathcal{E})^2/2E_n][\tfrac{3}{4}\langle z^2\rangle_{\lambda=0}+\tfrac{1}{2}\langle r^2\rangle_{\lambda=0}-(\langle z\rangle_{\lambda=0})^2]\ . \tag{45}$$

The remaining task is to compute $\langle r^2\rangle_{\lambda=0}$ and $\langle z^2\rangle_{\lambda=0}$. The details of their evaluations will be presented in Appendix B. Here we only quote the results:

$$\langle r^2\rangle_{\lambda=0}=(na_0/Z)^2\ (\tfrac{5}{2}n^2-\tfrac{3}{2}\langle\vec{L}^2\rangle_{\lambda=0}+\tfrac{1}{2})\ , \tag{46}$$

$$\langle z^2\rangle_{\lambda=0}=(na_0/Z)^2\ (\tfrac{5}{2}k^2+\tfrac{1}{2}\langle\vec{L}^2\rangle_{\lambda=0}-\tfrac{1}{2}m^2+1)\ , \tag{47}$$

where $\langle\vec{L}^2\rangle_{\lambda=0}$ is given by Eq. (22). Substituting Eqs. (46) and (47) into Eq. (45), we obtain

$$E^{(2)}=-(n^4a_0^3\mathcal{E}^2/16Z^4)(17n^2-9m^2-3k^2+19), \tag{48}$$

which is the same result as that obtained in Ref. 1.

IV. THIRD-ORDER STARK EFFECT

The extension of the method discussed in Sec. III to the third-order Stark effect is not trivial. We find it is more convenient to use a slightly modified form of Eq. (37):

$$\frac{\partial H_\lambda}{\partial\lambda}=-e\mathcal{E}z=\frac{3Ze^2}{4H_\lambda}e\mathcal{E}\tilde{A}_z+\frac{\lambda(e\mathcal{E})^2}{8H_\lambda}(7r^2+3z^2)+\frac{d}{dt}\tilde{G}'\ , \tag{49}$$

where

$$\tilde{A}_z=A_z-\frac{\lambda e\mathcal{E}}{2Ze^2}(r^2-z^2),\quad \frac{d\tilde{A}_z}{dt}=0\ , \tag{50}$$

and $\tilde{G}'$ is just Eq. (38) with $H_0\to H_\lambda$. Again the proof of Eq. (49) will be given in Appendix A. Now if we choose the state $\langle\xi'_\lambda|$ to be an eigenstate of both H_λ and $\tilde{A}_z$, then from Eqs. (35) and (49) we obtain[5]

$$\frac{\partial E'_\lambda}{\partial\lambda}=\frac{3Ze^2}{4E_\lambda}e\mathcal{E}\tilde{A}'_z+\lambda\frac{(e\mathcal{E})^2}{8E_\lambda}\langle 7r^2+3z^2\rangle_\lambda\ , \tag{51}$$

where

$$\langle\xi'_\lambda|\tilde{A}_z=\langle\xi'_\lambda|\tilde{A}'_z\ . \tag{52}$$

Equation (51) together with Eq. (34) is the basic equation to apply our perturbation theory.

To illustrate the advantage of this modification, consider the second-order effect. Differentiating Eq. (51) once with respect to λ and then setting $\lambda=0$, we obtain

$$2E^{(2)}=\frac{3Ze^2}{4}\left(-\frac{E^{(1)}}{E_n^2}\right)e\mathcal{E}A_z'+\frac{3Ze^2}{4E_n}e\mathcal{E}\left(\frac{\partial\tilde{A}'_z}{\partial\lambda}\right)_{\lambda=0}+\frac{(e\mathcal{E})^2}{8E_n}\langle 7r^2+3z^2\rangle_{\lambda=0}\ ,$$

or

$$E^{(2)}=[(e\mathcal{E})^2/2E_n][\tfrac{3}{4}\langle z^2\rangle_{\lambda=0}+\tfrac{1}{2}\langle r^2\rangle_{\lambda=0}-(\langle z\rangle_{\lambda=0})]^2 \tag{53}$$

which is just Eq. (45). However, we are able to obtain this result here without using the explicit form of G.

The third-order perturbation can be obtained by differentiating Eq. (51) twice with respect to λ and then setting $\lambda=0$:

$$3!E^{(3)}=[3(e\mathcal{E})^3/E_n^2]\langle z\rangle_{\lambda=0}[\tfrac{3}{4}\langle z^2\rangle_{\lambda=0}-(\langle z\rangle_{\lambda=0})]^2+[(e\mathcal{E})^2/8E_n](i/\hbar)\langle[G,11r^2+9z^2]\rangle_{\lambda=0}\ . \tag{54}$$

Here as in Sec. III, we need an explicit form of G at $\lambda=0$, which has the form of Eq. (42). In order to determine δG, we observe that the eigenvalue equation for $\tilde{A}_z$ [Eq. (52)] is quite similar to that for H_λ [Eq. (29)]. By following closely to the arguments given there, we can easily show that[5,6] [cf. Eq. (32)]

$$\frac{\partial\tilde{A}_z}{\partial\lambda}=\frac{\partial\tilde{A}'_z}{\partial\lambda}+\frac{1}{i\hbar}[G,\tilde{A}_z]\ , \tag{55}$$

or at $\lambda=0$,

$$\frac{i}{\hbar}[A_z, G]=\left(\frac{\partial \tilde{A}_z}{\partial \lambda}-\frac{\partial \tilde{A}_z'}{\partial \lambda}\right)_{\lambda=0}$$
$$= -(e\mathcal{E}/2Ze^2)[(r^2-z^2)-\langle(r^2-z^2)\rangle_{\lambda=0}] . \quad (56)$$

By using Eq. (38), we can easily show that

$$\frac{i}{\hbar}[A_z, \tilde{G}] = -\frac{e\mathcal{E}}{2Ze^2}(r^2-z^2)-\frac{a_0}{2Z}\left(\frac{3}{2}\vec{L}^2-L_z^2+1\right)\frac{e\mathcal{E}}{H_0} . \quad (57)$$

Therefore, from Eqs. (56) and (57), we infer the following condition for δG (Ref. 5):

$$\frac{i}{\hbar}[A_z, \delta G]= -\frac{3e\mathcal{E}}{2Ze^2}\left(\frac{na_0}{Z}\right)^2(\vec{L}^2-\langle\vec{L}^2\rangle_{\lambda=0}) , \quad (58)$$

which implies

$$\frac{i}{\hbar}\delta G=e\mathcal{E}\frac{3}{4Ze^2}\left(\frac{n^2a_0}{Z}\right)^2 i(\vec{A}\times\vec{L})_z+\frac{i}{\hbar}\delta G' , \quad (59)$$

since

$$[A_z, i(\vec{A}\times\vec{L})_z]= -(2/n^2)(\vec{L}^2-\langle\vec{L}^2\rangle_{\lambda=0}) . \quad (60)$$

Note that Eq. (58) cannot determine terms that commute with A_z, and $\delta G'$ is an arbitrary function of A_z and L_z, which is diagonal and does not contribute to our calculation here.

Now it is straightforward to show that

$$\langle[\tilde{G}, 11r^2+9z^2]\rangle_{\lambda=0}=i\hbar(e\mathcal{E}/E_n)$$
$$\times[\tfrac{51}{2}\langle r^2z\rangle_{\lambda=0}+\tfrac{9}{2}\langle z^3\rangle_{\lambda=0}$$
$$-11\langle z\rangle_{\lambda=0}\langle r^2\rangle_{\lambda=0}$$
$$-9\langle z\rangle_{\lambda=0}\langle z^2\rangle_{\lambda=0}] , \quad (61)$$

$$\frac{i}{\hbar}\langle[\delta G, r^2]\rangle_{\lambda=0}=e\mathcal{E}\frac{3}{2}\frac{1}{Ze^2}\left(\frac{na_0}{Z}\right)^3 n\langle z\rangle_{\lambda=0}\langle\vec{L}^2\rangle_{\lambda=0} , \quad (62)$$

$$\frac{i}{\hbar}\langle[\delta G, z^2]\rangle_{\lambda=0}= -e\mathcal{E}\frac{1}{2}\frac{1}{Ze^2}\left(\frac{na_0}{Z}\right)^3 n\langle z\rangle_{\lambda=0}\langle\vec{L}^2\rangle_{\lambda=0} . \quad (63)$$

Substituting Eqs. (61)–(63) into Eq. (54), we obtain

$$E^{(3)}= -\frac{1}{32}\frac{(e\mathcal{E})^3}{E_n^2}[17\langle r^2z\rangle_{\lambda=0}+3\langle z^3\rangle_{\lambda=0}-18\langle z\rangle_{\lambda=0}\langle z^2\rangle_{\lambda=0}$$
$$-\tfrac{46}{3}\langle r^2\rangle_{\lambda=0}\langle z\rangle_{\lambda=0}+16(\langle z\rangle_{\lambda=0})^3]$$
$$+\frac{(e\mathcal{E})^3}{4E_n}\frac{1}{Ze^2}\left(\frac{na_0}{Z}\right)^3 n\langle z\rangle_{\lambda=0}\langle\vec{L}^2\rangle_{\lambda=0} . \quad (64)$$

Here we only have to calculate $\langle r^2z\rangle_{\lambda=0}$ and $\langle z^3\rangle_{\lambda=0}$. Their evaluation will be presented in Appendix B. The results are

$$\langle r^2z\rangle_{\lambda=0}=\tfrac{5}{8}\left(\frac{na_0}{Z}\right)^3 nA_z'(7n^2-3\langle\vec{L}^2\rangle_{\lambda=0}+5) , \quad (65)$$

$$\langle z^3\rangle_{\lambda=0}=\tfrac{5}{8}\left(\frac{na_0}{Z}\right)^3 nA_z'(7k^2+3\langle\vec{L}^2\rangle_{\lambda=0}-3n^2+8) . \quad (66)$$

Therefore, we obtain the final result for the third-order Stark effect:

$$E^{(3)}=\tfrac{3}{32}(n^7a_0^5\mathcal{E}^3/Z^7e)k[23n^2+11m^2-k^2+39] , \quad (67)$$

which agrees with the result of Ref. 2. However, it appears that we obtain this result in a much simpler way than that of Ref. 2.

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APPENDIX A

In this appendix, we wish to prove the identities, Eqs. (37) and (49). Consider

$$\frac{d}{dt}\mu[(\vec{r}\cdot\vec{p})\vec{r}+\vec{r}(\vec{p}\cdot\vec{r})-x_i\vec{p}x_i]$$
$$=p^2\vec{r}+\vec{r}p^2-\frac{\mu Ze^2}{r}\vec{r}+\mu\lambda e[2(\vec{\mathcal{E}}\cdot\vec{r})\vec{r}-\vec{\mathcal{E}}r^2]$$
$$=2\mu(H_\lambda\vec{r}+\vec{r}H_\lambda)+3\mu Ze^2\frac{\vec{r}}{r}+\mu\lambda e[6(\vec{\mathcal{E}}\cdot\vec{r})\vec{r}-\vec{\mathcal{E}}r^2] , \quad (A1)$$

by using Heisenberg's equations of motion, Eqs. (27) and (28). Now from the definition of $\vec{A}$, Eq. (3), we have

$$\frac{\vec{r}}{r}=\vec{A}+\frac{\hbar}{\mu Ze^2}\frac{1}{2}(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})$$
$$=\vec{A}+\frac{\hbar}{\mu Ze^2}\left[\frac{\mu}{2}\frac{d}{dt}(\vec{r}\times\vec{L}-\vec{L}\times\vec{r})-\frac{\mu}{2}\left(\vec{r}\times\frac{d\vec{L}}{dt}-\frac{d\vec{L}}{dt}\times\vec{r}\right)\right]$$
$$=\vec{A}-\frac{\mu\lambda e}{\mu Ze^2}(\vec{r}(\vec{\mathcal{E}}\cdot\vec{r})-\vec{\mathcal{E}}r^2)$$
$$-\frac{1}{\mu Ze^2}\frac{\mu}{2}\frac{d}{dt}(2x_i\vec{p}x_i-(\vec{r}\cdot\vec{p})\vec{r}-\vec{r}(\vec{p}\cdot\vec{r})) . \quad (A2)$$

Substituting Eq. (A2) into Eq. (A1), and noting that

$$H_\lambda\vec{r}+\vec{r}H_\lambda=2H_\lambda\vec{r}+i\hbar\frac{d\vec{r}}{dt}$$
$$=2\vec{r}H_\lambda-i\hbar\frac{d\vec{r}}{dt} , \quad (A3)$$

we obtain

$$\vec{r} = -\frac{3\mu Ze^2}{4H_\lambda}\tilde{A} - \frac{\lambda e}{4H_\lambda}[3(\vec{\mathcal{E}}\cdot\vec{r})\vec{r} + 2\vec{\mathcal{E}}r^2] + \frac{d}{dt}[H_\lambda^{-1}(\tfrac{1}{2}x_i\vec{p}x_i - \tfrac{1}{8}(\vec{r}\cdot\vec{p})\vec{r} - \tfrac{1}{8}\vec{r}(\vec{p}\cdot\vec{r}) - \tfrac{1}{2}i\hbar\vec{r})] \quad \text{(A4)}$$

In terms of

$$\tilde{A}_z = A_z - (\lambda e\mathcal{E}/2Ze^2)(r^2 - z^2), \quad \text{(A5)}$$

we obtain Eq. (49). The extra term, $\frac{1}{2}i\hbar\langle z\rangle$, in Eq. (38) is added in order to guarantee that $\tilde{G}$ is a unitary operator. It can also be inferred from the condition[5] [letting $\lambda = 0$ in Eq. (32)]

$$\frac{i}{\hbar}[H_0, G] = \left(\frac{\partial H_\lambda}{\partial\lambda} - \frac{\partial E'_\lambda}{\partial\lambda}\right)_{\lambda=0} \quad \text{(A6)}$$

or

$$(i/\hbar)[H_0, \tilde{G}] = -e\mathcal{E}(z - \langle z\rangle). \quad \text{(A7)}$$

APPENDIX B: EVALUATION OF EXPECTATION VALUES

In this Appendix, we will demonstrate how to evaluate expectation values of operators without using the wave functions. We will denote by $\langle \mathcal{O}\rangle$ the expectation value of an operator $\mathcal{O}$ between the unperturbed states $|nk_1k_2\rangle$.

(i) From Eq. (A4), we have (letting $\lambda = 0$)

$$\vec{r} = -\frac{3\mu Ze^2}{4H_0}\vec{A} + \frac{d}{dt}\left(\frac{1}{H_0}\vec{X}\right), \quad \text{(B1)}$$

where

$$\vec{X} \equiv \tfrac{1}{2}x_i\vec{p}x_i - \tfrac{1}{8}(\vec{r}\cdot\vec{p})\vec{r} - \tfrac{1}{8}\vec{r}(\vec{p}\cdot\vec{r}) - \tfrac{1}{2}i\hbar\vec{r},$$

$$= \tfrac{1}{2}r^2\vec{p} - \tfrac{1}{4}(\vec{r}\cdot\vec{p})\vec{r} - \tfrac{3}{4}i\hbar\vec{r}. \quad \text{(B2)}$$

Therefore, we obtain immediately

$$\langle z\rangle = -(3\mu Ze^2/4E_n)A'_z = \tfrac{3}{2}(na_0/Z)k, \quad \text{(B3)}$$

by using Eqs. (19)–(21).

(ii) From the definition of $\vec{A}$, we have

$$\langle r\rangle = \langle\vec{r}\cdot\vec{A}\rangle + (a_0/Z)\langle\vec{L}^2 - (i/\hbar)\vec{r}\cdot\vec{p}\rangle,$$

$$= -(3Ze^2/4E_n)\langle\vec{A}^2\rangle + (a_0/Z)(\langle\vec{L}^2\rangle + \tfrac{3}{2}),$$

$$= (a_0/2Z)(3n^2 - \langle\vec{L}^2\rangle), \quad \text{(B4)}$$

where we have used Eq. (8)

$$\langle\vec{A}^2\rangle = 1 - 1/n^2 - (1/n^2)\langle\vec{L}^2\rangle, \quad \text{(B5)}$$

and

$$\langle\vec{r}\cdot\vec{p}\rangle = \left\langle\frac{\mu}{2}\frac{d\vec{r}^2}{dt} + \frac{3}{2}i\hbar\right\rangle = \tfrac{3}{2}i\hbar. \quad \text{(B6)}$$

(iii) From Eq. (B 1), we have

$$\langle\vec{r}^2\rangle = -\frac{3\mu Ze^2}{4E_n}\langle\vec{A}\cdot\vec{r}\rangle - \frac{1}{\mu E_n}\langle\vec{X}\cdot\vec{p}\rangle = \left(-\frac{3\mu Ze^2}{4E_n}\right)^2\langle\vec{A}^2\rangle - \frac{1}{\mu E_n}\langle\tfrac{1}{2}r^2p^2 - \tfrac{1}{4}(\vec{r}\cdot\vec{p})^2 - \tfrac{3}{4}i\hbar\vec{r}\cdot\vec{p}\rangle. \quad \text{(B7)}$$

By using Eqs. (B 4) and (B 5) and the identities

$$(\vec{r}\cdot\vec{p})^2 = r^2p^2 + i\hbar\vec{r}\cdot\vec{p} - \hbar^2\vec{L}^2, \quad \text{(B8)}$$

$$\langle r^2p^2\rangle = 2\mu E_n\langle r^2\rangle + 2\mu Ze^2\langle r\rangle, \quad \text{(B9)}$$

we obtain

$$\langle\vec{r}^2\rangle = \left(\frac{na_0}{Z}\right)^2(\tfrac{5}{2}n^2 - \tfrac{3}{2}\langle\vec{L}^2\rangle + \tfrac{1}{2}). \quad \text{(B10)}$$

(iv) To evaluate $\langle z^2\rangle$, we pick up the z component of Eq. (B 1) and multiply it by z and obtain

$$\langle z^2\rangle = -\frac{3Ze^2}{4E_n}\langle A_z z\rangle - \frac{1}{E_n}\langle X_z p_z\rangle = \left(-\frac{3Ze^2}{4E_n}\right)^2 A_z'^2 - \frac{1}{\mu E_n}[\tfrac{3}{8}\langle r^2p_z^2\rangle - \tfrac{1}{8}\langle z^2p^2\rangle + \tfrac{1}{8}\hbar^2(\langle\vec{L}^2\rangle - m^2 + 4)]$$

$$= \left(\frac{na_0}{Z}\right)^2(\tfrac{5}{2}k^2 + \tfrac{1}{2}\langle\vec{L}^2\rangle - \tfrac{1}{2}m^2 + 1), \quad \text{(B11)}$$

by using the following identities

$$2zp_z(\vec{r}\cdot\vec{p}) = z^2p^2 + r^2p_z^2 + i\hbar(\vec{r}\cdot\vec{p} - zp_z) - \hbar^2(\vec{L}^2 - L_z^2), \quad \text{(B12)}$$

$$\langle r^2p_z^2\rangle = 2\mu E_n\langle z^2\rangle + 2\mu Ze^2\langle z\rangle A'_z + \hbar^2(\langle\vec{L}^2\rangle - m^2 + 1), \quad \text{(B13)}$$

$$\langle z^2p^2\rangle = -\tfrac{2}{3}\mu E_n\langle z^2\rangle - \tfrac{2}{3}\langle r^2p_z^2\rangle + \tfrac{2}{3}\hbar^2(\langle\vec{L}^2\rangle - m^2 - \tfrac{1}{2}). \quad \text{(B 14)}$$

(v) From the identities

$$\hbar(\vec{A}\times\vec{L})_z = (z/r)(\vec{r}\cdot\vec{p}) - rp_z + (\hbar^2\vec{L}^2/\mu Ze^2)p_z, \quad \text{(B15)}$$

$$\langle rp_z\rangle = -(Z/n^2a_0)\langle z\vec{r}\cdot\vec{p}\rangle + \tfrac{7}{2}i\hbar A'_z, \quad \text{(B16)}$$

$$\langle i(\vec{A}\times\vec{L})_z\rangle = -A'_z, \quad \text{(B17)}$$

one obtains

$$\langle z\vec{r}\cdot\vec{p}\rangle = 2i\hbar\langle z\rangle. \quad \text{(B18)}$$

(vi) From the consideration of

$$\langle z^3/r\rangle = \langle z^2[A_z + (1/\mu Ze^2)(zp^2 - p_z\vec{r}\cdot\vec{p})]\rangle \quad \text{(B19)}$$

and the observation that

$$\langle z^2 p_z \vec{r}\cdot\vec{p}\rangle = \left\langle \left(\frac{\mu}{3}\frac{dz^3}{dt} + i\hbar z\right)(\vec{r}\cdot\vec{p})\right\rangle$$

$$= -\tfrac{1}{3}\langle z^3 p^2\rangle + \tfrac{1}{3}\mu Ze^2\langle z^3/r\rangle - 2\hbar^2\langle z\rangle \ , \tag{B20}$$

we obtain

$$\langle z^3/r\rangle = (Z/n^2 a_0)\langle z^3\rangle - \tfrac{3}{4}\langle z^2\rangle A_z' - \tfrac{3}{2}a_0/Z\langle z\rangle \ . \tag{B21}$$

(vii) To evaluate $\langle z^3\rangle$, one considers

$$\langle z^3\rangle = -(3Ze^2/4E_n)\langle A_z z^2\rangle - (1/\mu E_n)\langle 2X_z z p_z - i\hbar X_z\rangle$$

$$= -\tfrac{5}{8}(na_0/Z)^3 k(7k^2 + 3\langle \vec{L}^2\rangle - 3m^2 + 8) \tag{B22}$$

by using Eqs. (B 18) and (B 21).

(viii) Finally, to evaluate $\langle r^2 z\rangle$ and $\langle rz\rangle$, we consider

$$\langle r^2 z\rangle = -\frac{3Ze^2}{4E_n}\langle \vec{A}\cdot\vec{r}z\rangle - \frac{1}{\mu E_n}\langle (\vec{X}\cdot\vec{r})p_z + (\vec{X}\cdot\vec{p})z\rangle$$

$$= \left(\frac{na_0}{Z}\right)^2\left[\frac{7}{4}\frac{Z}{a_0}\langle rz\rangle - \left(\frac{2}{3}\langle \vec{L}^2\rangle - \frac{3}{2}\right)\langle z\rangle\right] \ . \tag{B23}$$

On the other hand, by considering

$$\langle \vec{r}^2\rangle A_z' = \langle r[z - (1/\mu Ze^2)r(zp^2 - p_z\vec{r}\cdot\vec{p})]\rangle \tag{B24}$$

one obtains

$$\langle rz\rangle = -\frac{4}{3}\langle r^2\rangle A_z' + \frac{4}{3}\frac{Z}{n^2 a_0}\langle r^2 z\rangle - \frac{2a_0}{Z}\langle z\rangle \ . \tag{B25}$$

Combining Eqs. (B 23) and (B 25), we have

$$\langle r^2 z\rangle = -\tfrac{5}{8}(na_0/Z)^3 k[7n^2 - 3\langle \vec{L}^2\rangle + 5] \ , \tag{B26}$$

$$\langle rz\rangle = (na_0/Z)^2 A_z'[\tfrac{5}{2}n^2 - \tfrac{1}{2}\langle \vec{L}^2\rangle + \tfrac{1}{2}] \ . \tag{B27}$$

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[1]For an excellent review of this subject, together with all earlier references, see the text by E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., London, England 1970), Chap. 17.

[2]M. A. El-Sherbini, Philos. Mag. 14, 384 (1932).

[3]J. Schwinger, lecture notes on Quantum Mechanics, Harvard University, 1952 (unpublished). I thank him for making these notes available to us.

[4]Since both $\vec{A}$ and $\vec{L}$ commute with H_0, the formal definition of $\vec{J}^{(a)}$ here is unambiguous. In computing the commutation relations between $\vec{J}$'s, H_0 behaves as a constant operator; when H_0 operates on a state, it gives the energy eigenvalue E_n of the state. The minus sign is introduced in the square root because we are interested in the bound state spectrum ($E_n < 0$) of hydrogenic atoms.

[5]We use the notation that, when eigenvalue notations [$\partial E_\lambda'/\partial\lambda$ in Eq. (32) and $\partial\tilde{A}'/\partial\lambda$ in Eq. (55)] or expectation value forms [$\langle z\rangle$ in Eq. (38), $\langle r^2 - z^2\rangle_{\lambda=0}$ in Eq. (56), and $\langle \vec{L}^2\rangle_{\lambda=0}$ in Eqs. (58) and (60)] appear in operator equations, they should be understood as the diagonal part of the corresponding operator in that particular base. For example, the notation $\langle \vec{L}^2\rangle_{\lambda=0}$ in Eq. (58) represents the diagonal part of $\vec{L}^2$ in the $|nk_1k_2\rangle$ representation, i.e.,

$$\langle \vec{L}^2\rangle_{\lambda=0} \to \tfrac{1}{2}[(-\mu Z^2 e^4/2\hbar^2 H_0)(1 - A_z^2) + L_z^2 - 1] \ .$$

[6]I thank Professor J. Schwinger for pointing out this identity to me and for his helpful comments concerning the determination of δG.