35

Perturbed Coulomb Problems via SO(2,1) Algebra

A Perturbed Coulomb Problems: The Conventional Approach with its Infinite Sums and Continuum Integrals: An Example: The Second-Order Stark Effect of the Hydrogen Atom Ground State

So far, we have not solved many perturbed Coulomb problems by conventional perturbation theory, that is, by the conventional radial and angular functions. The difficulty here is that perturbation terms which are functions of the radial coordinate, r, lead to an infinite number of nonzero matrix elements, connecting a bound state of definite, n, to all other bound states, as well as to the full spectrum of continuum states. The complete set of states includes both the bound states and the continuum states. The unit operator in this conventional basis is given by

$$1 = \sum_{n=1}^{\infty} \sum_{l,m} |nlm\rangle\langle nlm| + \int d\Omega_k \int_0^{\infty} dk k^2 |\vec{k}\rangle\langle\vec{k}|, \tag{1}$$

where the continuum states are the continuum solutions of the Coulomb problem, with energy, $\hbar^2 k^2/(2\mu)$, which in the limit $k \to \infty$ go over to plane wave states $\to \langle\vec{r}|\vec{k}\rangle = e^{i\vec{k}\cdot\vec{r}}/(2\pi)^{\frac{3}{2}}$. (These continuum Coulomb states will be discussed in detail in Chapter 42 in connection with our study of scattering theory.)

To illustrate the difficulties with the conventional radial Coulomb functions, let us look at a very simple perturbation problem: the second-order Stark effect of the

K. T. Hecht, *Quantum Mechanics*

hydrogen atom ground state. The Hamiltonian is

$$H = H^{0)} + H^{(1)} = H_{\text{Coulomb}} - e\mathcal{E}r\cos\theta, \tag{2}$$

where $\vec{\mathcal{E}}$ is the external electric field in the z direction. Conventional second-order perturbation theory gives

$$E^{(2)}_{n=1,l=0,m=0} = \sum_{n=2}^{\infty} \frac{|\langle n10|H^{(1)}|100\rangle|^2}{(E_1^{(0)} - E_n^{(0)})} + \int d\Omega_k \int_0^{\infty} dk k^2 \frac{|\langle \vec{k}|H^{(1)}|100\rangle|^2}{[E_1^{(0)} - \frac{\hbar^2 k^2}{2\mu}]}. \tag{3}$$

The needed matrix element between the hydrogen ground state and an arbitrary discrete excited state will be calculated later in this chapter. It is

$$\langle nlm|H^{(1)}|100\rangle = -\delta_{l1}\delta_{m0} e\mathcal{E}a_0 2^4 n^3 \frac{(n-1)^{n-3}}{(n+1)^{n+3}} \left[\frac{(n+1)n(n-1)}{3}\right]^{\frac{1}{2}}. \tag{4}$$

The needed matrix element between the hydrogenic ground state and a continuum state will be calculated in the mathematical appendix to Chapter 42. It is

$$\begin{aligned}\langle \vec{k}|H^{(1)}|100\rangle &= -\delta_{l1}\delta_{m0} e\mathcal{E} \frac{a_0^{\frac{5}{2}}}{(2\pi)^{\frac{3}{2}}} \frac{4\pi}{\sqrt{3}} Y_{lm}(\theta_k, \phi_k) \\ &\times \left[\frac{(\gamma^2+1)2\pi\gamma}{(1-e^{-2\gamma\pi})}\right]^{\frac{1}{2}} \frac{8i\gamma^5}{(\gamma^2+1)^3} e^{-2\gamma \tan^{-1}(1/\gamma)},\end{aligned} \tag{5}$$

where γ is the Coulomb parameter

$$\gamma = \frac{1}{ka_0}, \qquad a_0 = \frac{\hbar^2}{Z\mu e^2}, \tag{6}$$

and $\vec{k}$ is given by its magnitude, k, and direction specified by polar and azimuth angles, θ_k, ϕ_k. With these results, the second-order correction to the energy is

$$\begin{aligned}E^{(2)} &= -\left(\frac{e^2 a_0^2 \mathcal{E}^2}{\mu Z^2 e^4/\hbar^2}\right)\left(\sum_{n=2}^{\infty} \frac{2^9 n^9}{3} \frac{(n-1)^{2n-6}}{(n+1)^{2n+6}}\right. \\ &\left. + \int d\Omega_k Y_{10}^{*}(\theta_k, \phi_k) Y_{10}(\theta_k, \phi_k) \frac{512}{3} \int_0^{\infty} d\gamma \frac{\gamma^9}{(\gamma^2+1)^6} \frac{e^{-4\gamma \tan^{-1}(1/\gamma)}}{(1-e^{-2\gamma\pi})}\right) \\ &= -\left(\frac{e^2 a_0^2 \mathcal{E}^2}{\mu Z^2 e^4/\hbar^2}\right)\left(\sum_{n=2}^{\infty} \frac{2^9 n^9}{3} \frac{(n-1)^{2n-6}}{(n+1)^{2n+6}} + .418371\right) \\ &= -\left(\frac{e^2 a_0^2 \mathcal{E}^2}{\mu Z^2 e^4/\hbar^2}\right) 2.25,\end{aligned} \tag{7}$$

where the γ integral is best done numerically, and, as we shall see, the final result is given, in the appropriate units, by -(9/4), exactly. The infinite discrete sum converges quite rapidly. For example, the first five terms, through $n = 6$, give 1.792758, or a total of 2.211129 with the continuum contribution, which is within 1.7% of the exact result. We shall see in this chapter, however, we can arrive at the exact final result very simply by a perturbation expansion requiring a discrete sum of just two terms.

B The Runge–Lenz Vector as an ℓ Step Operator and the SO(4) Algebra of the Coulomb Problem

Before introducing the operators of an SO(2,1) algebra, which will be used to simplify the perturbation expansions for a perturbed Coulomb problem, let us look first at the commutator algebra of the quantum-mechanical operators arising from the known classical integrals for the Coulomb potential, the orbital angular momentum vector, $\vec{L}$, and the Runge–Lenz vector, $\vec{\mathcal{R}}$. It will be convenient to express all operators in dimensionless quantities through atomic units. Thus,

$$\vec{r}_{\text{phys.}} = a_0\vec{r}, \qquad \vec{p}_{\text{phys.}} = \frac{\hbar}{a_0}\vec{p}, \qquad \vec{L}_{\text{phys.}} = \hbar\vec{L}, \qquad \text{with } a_0 = \frac{\hbar^2}{Z\mu e^2},$$
$$H_{\text{phys.}} = \frac{Z^2\mu e^4}{\hbar^2}H, \qquad E_{\text{phys.}} = \frac{Z^2\mu e^4}{\hbar^2}\epsilon. \tag{8}$$

In these units, the Runge–Lenz vector (see problems 13 and 19) is

$$\vec{\mathcal{R}} = \frac{1}{2}\Big([\vec{p}\times\vec{L}] - [\vec{L}\times\vec{p}]\Big) - \frac{\vec{r}}{r} = \vec{r}(\vec{p}\cdot\vec{p}) - \vec{p}(\vec{r}\cdot\vec{p}) - \frac{\vec{r}}{r}, \tag{9}$$

with the properties

$$(\vec{\mathcal{R}}\cdot\vec{\mathcal{R}}) = 2H(\vec{L}\cdot\vec{L}+1)+1, \tag{10}$$

and

$$\vec{\mathcal{R}}\cdot\vec{L} = \vec{L}\cdot\vec{\mathcal{R}} = 0. \tag{11}$$

It was useful to define

$$\vec{V} = \frac{\vec{\mathcal{R}}}{\sqrt{(-2\epsilon)}} = n\vec{\mathcal{R}},$$

valid for negative-energy bound states. With this definition, eq. (10) becomes

$$(\vec{V}\cdot\vec{V}) + (\vec{L}\cdot\vec{L}) + 1 = \frac{1}{(-2\epsilon)} = n^2, \tag{12}$$

and the commutator algebra of the operators, $\vec{V}$, $\vec{L}$, is given by

$$[L_j, L_k] = i\epsilon_{jka}L_a, \qquad [L_j, V_k] = i\epsilon_{jka}V_a, \qquad [V_j, V_k] = i\epsilon_{jka}L_a. \tag{13}$$

If we define $L_{jk} = -L_{kj}$, with $j,k = 1,\ldots,4$ through

$$L_{jk} = \frac{1}{i}\left(x_j\frac{\partial}{\partial x_k} - x_k\frac{\partial}{\partial x_j}\right), \quad \text{with } L_1 = L_{23},\ L_2 = L_{31},\ L_3 = L_{12},$$
$$\text{and } V_j = L_{j4}, \tag{14}$$

the six operators, $\vec{L}$, $\vec{V}$, satisfy the same commutation relations as the six L_{jk}; i.e., the six operators, $\vec{L}$, $\vec{V}$, constitute infinitesimal rotation generators in an abstract 4-D space; i.e., they generate an SO(4) group, with a subgroup, SO(3), generated by the three components of $\vec{L}$.

It is useful to define the vector operators, $\vec{M}$ and $\vec{N}$, through

$$\vec{M} = \tfrac{1}{2}(\vec{L} + \vec{V}), \qquad \vec{N} = \tfrac{1}{2}(\vec{L} - \vec{V}), \tag{15}$$

where these operators satisfy the commutation relations of two *commuting* angular momentum operators

$$[M_j, M_k] = i\epsilon_{jka}M_a, \qquad [N_j, N_k] = i\epsilon_{jka}N_a, \qquad [M_j, N_k] = 0. \tag{16}$$

Eqs. (11) and (12) then lead to

$$\begin{aligned}(\vec{M}^2 - \vec{N}^2) &= \tfrac{1}{2}\left(\vec{L}\cdot\vec{V} + \vec{V}\cdot\vec{L}\right) = 0,\\ (\vec{M}^2 + \vec{N}^2) &= \tfrac{1}{2}(n^2 - 1).\end{aligned} \tag{17}$$

If the eigenvalues of the operators $\vec{M}^2$ and $\vec{N}^2$ are denoted by $j_1(j_1 + 1)$ and $j_2(j_2 + 1)$, respectively, these relations require

$$j_1 = j_2 = \tfrac{1}{2}(n - 1). \tag{18}$$

These angular momentum quantum numbers can thus be integral or half-integral. Two commuting angular momentum operators of this type generate a group which is a direct product of two SU(2) groups: $SU(2) \times SU(2)$. Because $\vec{L} = (\vec{M} + \vec{N})$, and we want to construct states of good orbital angular momentum, we want to use the vector-coupled basis $|[j_1 \times j_2]lm\rangle = |[\frac{1}{2}(n-1) \times \frac{1}{2}(n-1)]lm\rangle$, which is an eigenvector simultaneously of $\vec{L}^2$, L_0, and H, the latter with eigenvalue, $\epsilon = -1/2n^2$. The quantum number, n, also gives the eigenvalues of $\vec{M}^2$ and $\vec{N}^2$. Angular momentum vector coupling rules tell us the possible quantum numbers l range from 0, 1, ... to (n-1).

To understand the significance of the vector $\vec{V} = (\vec{M} - \vec{N})$, let us rewrite

$$\vec{V} = n\left(\vec{r}(\vec{p}\cdot\vec{p} - \frac{1}{r}) - \vec{p}(\vec{r}\cdot\vec{p})\right)$$

in terms of spherical coordinates, r, θ, ϕ. It will be sufficient to choose one component, e.g., the z component, which then has the form

$$\begin{aligned}\frac{V_0}{n} = r\cos\theta&\left(-\frac{\partial^2}{\partial r^2} - \frac{2}{r}\frac{\partial}{\partial r} + \frac{l(l+1)}{r^2} - \frac{1}{r}\right)\\ &+\left(\cos\theta\left(\frac{\partial}{\partial r}\right) + \frac{\sin\theta e^{i\phi}}{2r}L_- - \frac{\sin\theta e^{-i\phi}}{2r}L_+\right)\left(r\frac{\partial}{\partial r}\right).\end{aligned} \tag{19}$$

Using the known matrix elements of $L_\pm$ and of $\cos\theta$ and $\sin\theta e^{\pm i\phi}$, see e.g., eqs. (42)–(44) of Chapter 9, we see that action of this operator on a Coulomb eigenfunction yields

$$\begin{aligned}&V_0 R_{nl}(r)Y_{lm}(\theta,\phi) =\\ &n(l+1)\left[\left(-\frac{\partial}{\partial r} + \frac{l}{r} - \frac{1}{(l+1)}\right)R_{nl}(r)\right]\sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}}\,Y_{(l+1)m}\\ &+nl\left[\left(+\frac{\partial}{\partial r} + \frac{(l+1)}{r} - \frac{1}{l}\right)R_{nl}(r)\right]\sqrt{\frac{[l^2 - m^2]}{(2l+1)(2l-1)}}\,Y_{(l-1)m}.\end{aligned} \tag{20}$$

Rewriting the radial function in terms of the one-dimensionalized radial function, $R_{nl}(r) = u_{nl}(r)/r$, and introducing the Clebsch–Gordan coefficients, $\langle lm10|(l \pm 1)m\rangle$ (see the table at the end of Chapter 28), this can be rewritten as

$$
\begin{aligned}
&V_0 R_{nl}(r) Y_{lm}(\theta,\phi) = \\
&n(l+1)\frac{1}{r}\left[\left(-\frac{\partial}{\partial r}+\frac{(l+1)}{r}-\frac{1}{(l+1)}\right)u_{nl}(r)\right] \\
&\times\sqrt{\frac{(l+1)}{(2l+3)}}\langle lm10|(l+1)m\rangle Y_{(l+1)m} \\
&-nl\frac{1}{r}\left[\left(+\frac{\partial}{\partial r}+\frac{l}{r}-\frac{1}{l}\right)u_{nl}(r)\right]\sqrt{\frac{l}{(2l-1)}}\langle lm10|(l-1)m\rangle Y_{(l-1)m} \\
&= n(l+1)\frac{1}{r}\Big(O_+(l+1)u_{nl}(r)\Big)\sqrt{\frac{(l+1)}{(2l+3)}}\langle lm10|(l+1)m\rangle Y_{(l+1)m} \\
&-nl\frac{1}{r}\Big(O_-(l)u_{nl}(r)\Big)\sqrt{\frac{l}{(2l-1)}}\langle lm10|(l-1)m\rangle Y_{(l-1)m}, \qquad (21)
\end{aligned}
$$

where the operators $O_+(l+1)$ and $O_-(l)$ are the l step operators introduced in Chapter 10 to construct the radial Coulomb eigenfunctions. Finally, using the operators, $\mathcal{O}_+(l+1)$ and $\mathcal{O}_-(l)$, which construct normalized radial functions [see eq. (13) of Chapter 10], we have

$$
\begin{aligned}
&V_0\left[\frac{1}{r}u_{nl}(r)\right]Y_{lm}(\theta,\phi) = \\
&\sqrt{(l+1)[n^2-(l+1)^2]}\frac{1}{r}\mathcal{O}_+(l+1)u_{nl}(r)\frac{\langle lm10|(l+1)m\rangle}{\sqrt{(2l+3)}}Y_{(l+1)m} \\
&-\sqrt{l[n^2-l^2]}\frac{1}{r}\mathcal{O}_-(l)u_{nl}(r)\frac{\langle lm10|(l-1)m\rangle}{\sqrt{(2l-1)}}Y_{(l-1)m}, \qquad (22)
\end{aligned}
$$

where $(1/r)[\mathcal{O}_+(l+1)u_{nl}(r)]$ gives the normalized $R_{n(l+1)}(r)$, and similarly for $(1/r)[\mathcal{O}_-(l)u_{nl}(r)]$. Recalling the definition of the reduced matrix elements

$$
\langle nl'm|V_0|nlm\rangle = \frac{\langle lm10|l'm\rangle}{\sqrt{(2l'+1)}}\langle nl'\|\vec{V}\|nl\rangle,
$$

we see

$$
\begin{aligned}
\langle n(l+1)\|\vec{V}\|nl\rangle &= \sqrt{(l+1)[n^2-(l+1)^2]}, \\
\langle n(l-1)\|\vec{V}\|nl\rangle &= -\sqrt{l[n^2-l^2]}. \qquad (23)
\end{aligned}
$$

These equations give the only nonzero matrix elements of $\vec{V}$. We note that the properly normalized Runge–Lenz vector operator gives the l step operators in the subspace of a definite principal quantum number, n. Because the components of $\vec{L}$ furnish the m step operators for a fixed l; the operators $\vec{V}$ and $\vec{L}$ can serve to construct all n^2 states of a definite n, starting with the maximum possible $l = m = (n-1)$.

Although we have achieved our aim of finding the meaning of $\vec{V}$, we could have arrived at the above reduced matrix elements of $\vec{V}$ by using the angular momen-

tum–coupled basis $|[\frac{1}{2}(n-1)\times\frac{1}{2}(n-1)]lm\rangle$, in which the angular momentum eigenvectors of $\vec{M}$ are coupled to the angular momentum eigenvectors of $\vec{N}$ to resultant good orbital angular momentum of definite l, m. With $\vec{L}=\vec{M}+\vec{N}$, and $\vec{V}=\vec{M}-\vec{N}$, the reduced matrix elements of $\vec{L}$ and $\vec{V}$ follow from the reduced matrix elements of $\vec{M}$ and $\vec{N}$ via a simple unitary 9-j coefficient [see eq. (42) of Chapter 34]. Recall the vector $\vec{M}$ is a spherical tensor of spherical rank 1 in the $\vec{M}$ space, but because it does not act on the $\vec{N}$ space, it can be thought of as multiplied by the number 1, a spherical tensor of rank 0 in the $\vec{N}$ space. Thus,

$$\begin{aligned}
&\langle[j_1 j_2]l'\|\vec{M}\pm\vec{N}\|[j_1 j_2]l\rangle\\
&\equiv\langle[\tfrac{1}{2}(n-1)\ \tfrac{1}{2}(n-1)]l'\|\vec{M}\pm\vec{N}\|[\tfrac{1}{2}(n-1)\ \tfrac{1}{2}(n-1)]l\rangle\\
&=\tfrac{1}{2}\sqrt{(2l'+1)(n-1)(n+1)}\left[U\begin{pmatrix}\frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l\\ 1 & 0 & 1\\ \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l'\end{pmatrix}\right.\\
&\left.\pm U\begin{pmatrix}\frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l\\ 0 & 1 & 1\\ \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l'\end{pmatrix}\right]\\
&=\tfrac{1}{2}\sqrt{(2l'+1)(n-1)(n+1)}\Big(1\pm(-1)^{l'+l}\Big)\\
&\qquad\times\left[U\begin{pmatrix}\frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l\\ 1 & 0 & 1\\ \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l'\end{pmatrix}\right],
\end{aligned}\tag{24}$$

where we have used the reduced matrix elements,

$$\langle j'\|1\|j\rangle=\delta_{jj'}\sqrt{(2j+1)},\qquad\langle j'\|\vec{J}\|j\rangle=\delta_{jj'}\sqrt{(2j+1)j(j+1)},$$

valid for any angular momentum operator [see eqs. (4) and (7) of Chapter 32], where now $\vec{J}$ is either $\vec{M}$ or $\vec{N}$ and $j=\frac{1}{2}(n-1)$ for both. In the last step of the above equation, we have also used a symmetry property of the 9-j coefficent, involving interchange of columns 1 and 2. Finally, the unitary 9-j coefficient with one angular momentum, j_4, of zero can be replaced by a unitary Racah coefficient [see eq. (38) of Chapter 34], to yield

$$\begin{aligned}
&\langle[\tfrac{1}{2}(n-1)\ \tfrac{1}{2}(n-1)]l'\|\vec{M}\pm\vec{N}\|[\tfrac{1}{2}(n-1)\ \tfrac{1}{2}(n-1)]l\rangle=\\
&\tfrac{1}{2}\sqrt{(2l'+1)(n-1)(n+1)}(-1)^{l'-l}U(\tfrac{1}{2}(n-1)\tfrac{1}{2}(n-1)l'1;l\tfrac{1}{2}(n-1))\\
&\quad\times\Big(1\pm(-1)^{l+l'}\Big).
\end{aligned}\tag{25}$$

We see at once $\vec{L}=\vec{M}+\vec{N}$ has only diagonal matrix elements with $l'=l$, whereas $\vec{V}=\vec{M}-\vec{N}$ has zero diagonal matrix element with $l'=l$. (This can, of course, also be seen from the negative parity of the operator $\vec{V}$.) The Racah coefficients, with one $j=1$, are tabulated as algebraic functions of the possible angular momentum quantum numbers (see the angular momentum references at the end of Chapter 28). Putting in these values, we obtain the above results for $\langle nl'\|\vec{V}\|nl\rangle$, and the expected

$$\langle nl'\|\vec{L}\|nl\rangle=\delta_{l'l}\sqrt{(2l+1)l(l+1)}.\tag{26}$$

C The SO(2,1) Algebra

So far, the six operators, $\vec{V}$ and $\vec{L}$, can be used to generate the states and matrix elements in the n^2-dimensional subspace of a definite bound state of the hydrogen atom. To obtain general expressions for the matrix elements of radial functions, we still need to construct operators that can raise or lower the principal quantum number, n. For this purpose, we introduce the three operators, useful also for general central force potentials,

$$\begin{aligned} T_1 &= \tfrac{1}{2}\Big(rp_r^2 + \frac{l(l+1)}{r} - r\Big) \\ T_2 &= rp_r \\ T_3 &= \tfrac{1}{2}\Big(rp_r^2 + \frac{l(l+1)}{r} + r\Big), \end{aligned} \tag{27}$$

with

$$p_r = \frac{1}{i}\Big(\frac{\partial}{\partial r} + \frac{1}{r}\Big), \tag{28}$$

where r is again the dimensionless $r = r_{\text{phys.}}/a_0$. These T_i satisfy the SO(2,1) commutation relations

$$[T_1, T_2] = -iT_3, \qquad [T_2, T_3] = iT_1, \qquad [T_3, T_1] = iT_2, \tag{29}$$

or in terms of $T_\pm = (T_1 \pm iT_2)$

$$[T_3, T_\pm] = \pm T_\pm, \qquad \text{but} \quad [T_+, T_-] = -2T_3. \tag{30}$$

Except for one minus sign, these operators would be standard angular momentum operators. (The eigenvectors and operator matrix elements of these T_i were studied in problem 23.) These T_i, however, are hermitian operators not with respect to the standard volume element measure, $d\Omega dr r^2$, but instead with respect to the measure, $d\Omega dr r$. For example,

$$\begin{aligned} &\int\int d\Omega \int_0^\infty dr r \psi_1^* \Big(T_2 \psi_2\Big) = \int\int d\Omega \int_0^\infty dr r \psi_1^* \frac{1}{i}\Big(r\frac{\partial}{\partial r} + 1\Big)\psi_2 \\ &= \int\int d\Omega \Big(\frac{1}{i} r^2 \psi_1^* \psi_2 |_0^\infty + \Big(-\int_0^\infty dr \psi_2 \frac{1}{i}\frac{\partial}{\partial r}\Big(r^2 \psi_1^*\Big) + \int_0^\infty dr \psi_2 \frac{r}{i}\psi_1^*\Big) \\ &= -\int\int d\Omega \Big(\int_0^\infty dr \psi_2 \frac{r}{i}\psi_1^* + \int_0^\infty dr r^2 \psi_2 \frac{1}{i}\frac{\partial \psi_1^*}{\partial r}\Big) \\ &= \int\int d\Omega \Big(\int_0^\infty dr r \psi_2 \Big(T_2 \psi_1\Big)\Big)^*. \end{aligned} \tag{31}$$

The three T_i commute with the generalized $\vec{T}^2$ or SO(2,1) Casimir operator, C, defined by

$$\begin{aligned} C &= T_3^2 - T_1^2 - T_2^2 = (T_3 - T_1)(T_3 + T_1) - [T_3, T_1] - T_2^2 \\ &= r^2 p_r^2 + l(l+1) - irp_r - (rp_r)(rp_r) = l(l+1). \end{aligned} \tag{32}$$

In a basis in which both C and T_3 are diagonal,

$$C|ql) = l(l+1)|ql),$$

$$T_3 = q|ql), \tag{33}$$

the spectrum of allowed q values is given by a ladder of values starting with a minimum q value (see problem 23)

$$q = q_{\text{min.}} + n_r = (l+1) + n_r, \qquad \text{with} \quad n_r = 0, 1, 2, \ldots, \infty, \tag{34}$$

so the eigenvalue, q, of the operator T_3 can be identified with the principal quantum number $n = l + 1 + n_r$, and the nonzero matrix elements of $\vec{T}$ are given by

$$\begin{aligned} (ql|T_3|ql) &= q = n, \\ ((q-1)l|T_-|ql) &= \sqrt{(q+l)(q-l-1)}, \\ ((q+1)l|T_+|ql) &= \sqrt{(q-l)(q+l+1)}. \end{aligned} \tag{35}$$

(See problem 23.) Note: T_- annihilates the state with $q = (l+1)$, and T_+ can act as step-up operator to create states with $q = n > (l+1)$.

D The Dilation Property of the Operator, T_2

For the ordinary angular momentum algebra, the operator $e^{i\phi L_2}$ acted as a rotation operator. For the SO(2,1) algebra, the corresponding operator, e^{iaT_2}, acts as a dilation operator. Here, the parameter, a, like ϕ, is a real number. This dilation or stretching property follows because e^{iaT_2} acting on an arbitrary function of r yields

$$e^{iaT_2}F(r) = e^{a(r\frac{d}{dr}+1)}F(r) = e^a F(e^a r). \tag{36}$$

This relation follows if $F(r)$ can be expanded in an infinite series,

$$F(r) = c_0 + \sum_{n=1}^{\infty}(c_{-n}/r^n + c_n r^n),$$

because

$$e^{ar\frac{d}{dr}}r^{\pm n} = \sum_k \frac{a^k}{k!}\left(r\frac{d}{dr}\right)^k r^{\pm n} = \left(\sum_k \frac{(\pm an)^k}{k!}\right)r^{\pm n} = e^{\pm an}r^{\pm n} = \left(e^a r\right)^{\pm n}. \tag{37}$$

We shall also need the transformation of operators, O, via the unitary operator, e^{iaT_2}

$$e^{iaT_2}Oe^{-iaT_2} = \sum_n \frac{(ia)^n}{n!}[T_2,[T_2,[T_2,\ldots[T_2,O]\ldots]]]_n, \tag{38}$$

where the expansion is in terms of the n^{th} commutator of T_2 with the operator, O (for a derivation, see eqs. (23)–(25) of Chapter 16). For example, if $O = T_3$, we see that

$$[T_2,[T_2,[T_2,\ldots[T_2,T_3]\ldots]]]^{2n+1} = i^{2n+1}T_1, \tag{39}$$

for a commutator with an odd number of T_2's, whereas

$$[T_2,[T_2,[T_2,\ldots[T_2,T_3]\ldots]]]^{2n} = i^{2n}T_3, \tag{40}$$

for a commutator with an even number of T_2's. We therefore obtain

$$e^{iaT_2}T_3e^{-iaT_2} = \cosh aT_3 - \sinh aT_1, \tag{41}$$

and, similarly,

$$e^{iaT_2}T_1e^{-iaT_2} = \cosh aT_1 - \sinh aT_3. \tag{42}$$

Also, with $r = T_3 - T_1$,

$$e^{iaT_2}re^{-iaT_2} = e^a r, \tag{43}$$

and

$$e^{iaT_2}p_re^{-iaT_2} = e^{-a}p_r. \tag{44}$$

From these last two relations, the dilation transformation properties of simple functions of r and p_r can be obtained.

E The Zeroth-Order Energy Eigenvalue Problem for the Hydrogen Atom: Stretched States

The zeroth-order hydrogen atom eigenvalue problem can be written in terms of the SO(2,1) operators T_i. Keeping in mind the natural measure for these operators is $d\Omega dr r$ (rather than the conventional $d\Omega dr r^2$), the zeroth-order energy eigenvalue problem can be rewritten as

$$\begin{aligned}
0 &= \int d\vec{r}\Psi^*(H-\epsilon)\Psi \\
&= \int\int d\Omega\int_0^\infty dr r\Psi^*(rH - r\epsilon)\Psi \\
&= \int\int d\Omega\int_0^\infty dr r\Psi^*\left(\tfrac{1}{2}\left(rp_r^2 + \frac{\vec{L}^2}{r}\right) - 1 - r\epsilon\right)\Psi \\
&= \int\int d\Omega\int_0^\infty dr r\Psi^*\left(\tfrac{1}{2}r\left(-\frac{\partial^2}{\partial r} - \frac{2}{r}\frac{\partial}{\partial r} + \frac{l(l+1)}{r^2}\right) - 1 - r\epsilon\right)\Psi \\
&= \int\int d\Omega\int_0^\infty dr r\Psi^*\left(\tfrac{1}{2}(T_3+T_1) - \epsilon(T_3 - T_1) - 1\right)\Psi.
\end{aligned} \tag{45}$$

Although we have succeeded in rewriting the operator $r(H-\epsilon)$ in terms of the generators T_3 and T_1, these cannot be made simultaneously diagonal. To eliminate the unwanted T_1, we shall stretch the states Ψ with the dilation operator. By inserting unit operators, expressed through $1 = e^{-iaT_2}e^{iaT_2}$, in the appropriate places, the above eigenvalue integral can be rewritten as

$$\begin{aligned}
0 &= \int d\vec{r}\Psi^*(H-\epsilon)\Psi \\
&= \int\int d\Omega\int_0^\infty dr r\left(e^{iaT_2}\Psi\right)^*\Big[e^{iaT_2}\left(\tfrac{1}{2}(T_3+T_1)\right.
\end{aligned}$$

$$
\begin{aligned}
&\quad - \epsilon(T_3 - T_1) - 1\Big)e^{-iaT_2}\Big]\Big(e^{iaT_2}\Psi\Big) \\
&= \int_0^\infty drr\Big(e^{iaT_2}R_{nl}(r)\Big)^*\Bigg(\Big[(\tfrac{1}{2} - \epsilon)\cosh a - (\tfrac{1}{2} + \epsilon)\sinh a\Big]T_3 \\
&+ \Big[(\tfrac{1}{2} + \epsilon)\cosh a - (\tfrac{1}{2} - \epsilon)\sinh a\Big]T_1 - 1\Bigg)\Big(e^{iaT_2}R_{nl}(r)\Big), \qquad (46)
\end{aligned}
$$

where we have assumed the angular part of Ψ is a spherical harmonic of definite l and m. By choosing the real number, a, such that the coefficient of the T_1 term in the last line of the above relation is set equal to zero, the radial part of $(e^{iaT_2}\Psi)$ will have been transformed into an eigenfunction of T_3 and C. This result is achieved by choosing the parameter, a, such that

$$
\Big[(\tfrac{1}{2} + \epsilon)\cosh a - (\tfrac{1}{2} - \epsilon)\sinh a\Big] = 0, \qquad (47)
$$

which, for bound states, with negative ϵ, leads to

$$
e^{2a} = -\frac{1}{2\epsilon} = +n^2, \qquad (48)
$$

so

$$
e^a = n \qquad \text{and} \qquad \Big[(\tfrac{1}{2} - \epsilon)\cosh a - (\tfrac{1}{2} + \epsilon)\sinh a\Big] = \frac{1}{n} \qquad (49)
$$

for a bound state with $\epsilon = -1/2n^2$. The above eigenvalue equation then becomes

$$
\begin{aligned}
0 &= \int\int d\Omega \int_0^\infty drr\Psi^*(rH - r\epsilon)\Psi \\
&= \int_0^\infty drr\Big(e^{iaT_2}R_{nl}(r)\Big)^*\Big(\frac{1}{n}T_3 - 1)\Big)\Big(e^{iaT_2}R_{nl}(r)\Big) \\
&= |\mathcal{N}|^2\int_0^\infty drr\psi_{ql}^*\Big(\frac{1}{n}T_3 - 1\Big)\psi_{ql}, \qquad (50)
\end{aligned}
$$

which leads to the eigenvalue equation

$$
(T_3 - n)\psi_{ql} = (q - n)\psi_{ql} = 0, \qquad (51)
$$

so q can be identified with the conventional principal quantum number, n. We previously found that $q = q_{\min.} + n_r = (l + 1) + n_r$, which agrees with this result. In the above, we have named the stretched state

$$
\Big(e^{iaT_2}R_{nl}(r)\Big) = \mathcal{N}\psi_{ql}, \qquad (52)
$$

where $\psi_{q=n,l}$ is the normalized eigenfunction of the hermitian operator T_3 and the full 3-D function $\psi_{nl}(r)Y_{lm}(\theta, \phi) \equiv \Psi_{nlm}(\vec{r})$ is normalized with the new measure $d\Omega drr$. Because of this change of measure, the normalization is not preserved by the unitary dilation operator e^{iaT_2}. The normalization factor, $\mathcal{N}$, can be derived from

$$
1 = \int_0^\infty drr^2 R_{nl}(r)^* R_{nl}(r)
$$

$$= \int_0^\infty dr r \left(e^{iaT_2} R_{nl}(r)\right)^* \left(e^{iaT_2} r e^{-iaT_2}\right)\left(e^{iaT_2} R_{nl}(r)\right)$$
$$= \int_0^\infty dr r \mathcal{N}^* \psi_{nl}^*(r)\left(nr\right)\mathcal{N}\psi_{nl}(r) = |\mathcal{N}|^2 \int_0^\infty dr r \psi_{nl}^*(r) n(T_3 - T_1)\psi_{nl}(r)$$
$$= |\mathcal{N}|^2 n^2 \int_0^\infty dr r \psi_{nl}(r)^* \psi_{nl}(r) = |\mathcal{N}|^2 n^2, \tag{53}$$

where we have used the eigenvalue eq. (51) and the fact that T_1 has no matrix elements diagonal in n. We can therefore choose

$$\mathcal{N} = \frac{1}{n}. \tag{54}$$

Henceforth, we shall use the notations,

$$\psi_{q=n,l}(r), \quad \text{or} \quad \Psi_{q=n,lm}(\vec{r}) = \psi_{q=n,l}(r) Y_{lm}(\theta, \phi),$$

for the normalized stretched eigenfunctions and retain the $R_{nl}(r)Y_{lm}(\theta, \phi)$ for the conventional normalized bound-state eigenfunctions. To avoid confusion between the two conventions, we shall use caret notation for state vectors and matrix elements for the conventional hydrogenic states, but will use round parentheses for the state vectors and matrix elements of the stretched states. Thus, for an operator, O, a function of $\vec{r}$ and/or $\vec{p}$,

$$\int\int d\Omega \int_0^\infty dr r^2 (R_{n'l'}(r) Y_{l'm'}(\theta, \phi))^* O R_{nl}(r) Y_{lm}(\theta, \phi) \equiv \langle n'l'm'|O|nlm\rangle, \tag{55}$$

but for the analagous operator, $\tilde{O} \equiv e^{iaT_2} O e^{-iaT_2}$,

$$\int\int d\Omega \int_0^\infty dr r \Psi_{n'l'm'}^*(\widetilde{rO})\Psi_{nlm} \equiv (n'l'm'|(\widetilde{rO})|nlm). \tag{56}$$

[We have already anticipated this change of notation in our discussion of the matrix elements of the SO(2,1) operators T_i in eq. (35), where we have used round parentheses.] We can construct the explicit functional dependence of the $\psi_{ql}(r)$, via the explicit relation, $T_-|q = q_{\min.} = (l+1), l) = 0$, and subsequent successive action with T_+. Using

$$T_\pm = (T_1 \pm iT_2) = (T_1 - T_3) \pm iT_2 + T_3 = -r \pm \left(r\frac{\partial}{\partial r} + 1\right) + T_3, \tag{57}$$

the relation

$$T_-|q = q_{\min.} = (l+1), l) = 0 \qquad \text{leads to}$$
$$\left(-r - r\frac{\partial}{\partial r} - 1 + (l+1)\right)\psi_{q=(l+1),l}(r) = 0, \tag{58}$$

so

$$r\frac{d\psi_{(l+1),l}}{dr} = (l - r)\psi_{(l+1),l}, \tag{59}$$

with solution (normalized with the measure drr),

$$\psi_{q=(l+1),l}(r) = \frac{2^{l+1}}{\sqrt{(2l+1)!}} r^l e^{-r}. \tag{60}$$

States with values of $q > q_{\min.}$ can be obtained with successive action of T_+, with

$$\begin{aligned} |(q+1)l) &= \frac{1}{\sqrt{(q-l)(q+l+1)}} T_+ |ql) \\ \psi_{(q+1)l}(r) &= \frac{1}{\sqrt{(q-l)(q+l+1)}} \Big(r\frac{d}{dr} - r + q + 1\Big)\psi_{ql}(r), \end{aligned} \tag{61}$$

or

$$\begin{aligned} \psi_{ql}(r) &= \left[\frac{1}{1\cdot 2\cdots(q-l-1)\cdot(2l+2)(2l+3)\cdots(q+l)}\right]^{\frac{1}{2}} \Big(r\frac{d}{dr} - r + q\Big) \\ &\quad \times \Big(r\frac{d}{dr} - r + q - 1\Big)\cdots\Big(r\frac{d}{dr} - r + l + 3\Big)\Big(r\frac{d}{dr} - r + l + 2\Big)\psi_{q=(l+1)l}(r) \\ &= \sqrt{\frac{(2l+1)!}{(q+l)!(q-l-1)!}} \Big(r\frac{d}{dr} - r + q\Big)\Big(r\frac{d}{dr} - r + q - 1\Big)\cdots \\ &\quad \cdots\Big(r\frac{d}{dr} - r + l + 3\Big)\Big(r\frac{d}{dr} - r + l + 2\Big)\psi_{q=(l+1)l}(r). \end{aligned} \tag{62}$$

Using the identity

$$\Big(r\frac{d}{dr} - r + \alpha\Big)\psi(r) = e^r\Big(r\frac{d}{dr} + \alpha\Big)e^{-r}\psi(r), \tag{63}$$

and the fact that $(r\frac{d}{dr} + \alpha)$ commutes with $(r\frac{d}{dr} + \beta)$, the function $\psi_{ql}(r)$ can be rewritten (note the reversal of the operator order),

$$\begin{aligned} \psi_{ql}(r) &= \sqrt{\frac{(2l+1)!}{(q+l)!(q-l-1)!}} e^r \Big(r\frac{d}{dr} + l + 2\Big)\Big(r\frac{d}{dr} + l + 3\Big)\cdots \\ &\quad \cdots\Big(r\frac{d}{dr} + q - 1\Big)\Big(r\frac{d}{dr} + q\Big)e^{-r}\psi_{q=(l+1)l}(r) \\ &= \sqrt{\frac{(2l+1)!}{(q+l)!(q-l-1)!}} e^r \frac{1}{r^{l+1}}\frac{d}{dr}\frac{r^{l+2}}{r^{l+2}}\frac{d}{dr}\cdots\frac{d}{dr}\frac{r^{q-1}}{r^{q-1}}\frac{d}{dr} r^q e^{-r} \\ &\quad \times \frac{2^{l+1}}{\sqrt{(2l+1)!}} r^l e^{-r}, \end{aligned} \tag{64}$$

where we have made repeated use of the operator identity

$$\Big(r\frac{d}{dr} + \alpha\Big) = \frac{1}{r^{\alpha-1}}\frac{d}{dr} r^\alpha, \tag{65}$$

with $\alpha = l+2, l+3, \ldots, \alpha = q$. Simplifying, the above equation leads to the expression

$$\psi_{q,l}(r) = \frac{2^{l+1}}{\sqrt{(q+l)!(q-l-1)!}} e^r \frac{1}{r^{l+1}}\frac{d^{q-l-1}}{dr^{q-l-1}}\Big(r^{q+l}e^{-2r}\Big). \tag{66}$$

As a final remark to this section, we note that the stretched states with $q = n$, eigenstates of the operator, T_3, apply to the bound states of the hydrogen atom only, with negative ϵ. For the continuum states with $\epsilon > 0$, the requirement, $e^{2a} = -(1/2\epsilon)$ of eq. (48) cannot be met with a real value for a, and hence a unitary stretching operator e^{iaT_2}. In this case, however, e^a can be chosen such that the stretched states are eigenstates of the operator, T_1, by choosing a real parameter, a, such that the coefficient of T_3 in eq. (46) is set equal to zero, viz.,

$$(\tfrac{1}{2} - \epsilon)\cosh a - (\tfrac{1}{2} + \epsilon)\sinh a = 0, \tag{67}$$

leading to

$$e^{2a} = +\frac{1}{2\epsilon} = \frac{1}{(ka_0)^2} = \gamma^2, \tag{68}$$

where γ is the Coulomb parameter introduced in eq. (6). Now the zeroth order equation becomes

$$\begin{aligned} &\left(\frac{1}{\gamma}T_1 - 1\right)\left(e^{iaT_2}R_{\gamma,l}(r)\right) = 0, \\ &(T_1 - \gamma)\mathcal{N}_\gamma \psi_{\gamma,l}(r) = 0. \end{aligned} \tag{69}$$

The important point, however, is the following: The states $\psi_{nl}(r)$ and the $\psi_{\gamma,l}(r)$ belong to different irreducible representations of the SO(2,1) group. Each forms a complete set of its own. Perturbation theory for the bound states will not connect the ψ_{nl} to the $\psi_{\gamma,l}$.

F Perturbations of the Coulomb Problem

For a perturbed hydrogenic atom problem, it will be useful to transcribe the Schrödinger equation for the full Hamiltonian into the stretched-state basis. The SO(2,1) basis will be particularly useful for spherically symmetric perturbations, where l and m will be good quantum numbers to all orders. In that case [case (1) of Chapter 23], the spherical, nlm, is the symmetry adapted or proper basis; and therefore nondegenerate perturbation theory can be used. No connections exist from lm to states with $l' \neq l, m' \neq m$. For that case, the Schrödinger equation for the full Hamiltonian

$$\begin{aligned} 0 &= r(H - \epsilon)R_{nl}(r) \\ &= r\Big[(H^{(0)} + H^{(1)} + H^{(2)} + \cdots) - (\epsilon^{(0)} + \epsilon^{(1)} + \epsilon^{(2)} + \cdots)\Big]R_{nl}(r) \\ &= \Bigg(\Big[\tfrac{1}{2}(rp_r^2 + \frac{(l(l+1)}{r}) - 1 - r\epsilon^{(0)}\Big] \\ &\qquad + \Big[(rH^{(1)} - r\epsilon^{(1)}) + (rH^{(2)} - r\epsilon^{(2)}) + \cdots\Big]\Bigg)R_{nl}(r) \end{aligned} \tag{70}$$

can be transcribed to stretched form by acting on the above with e^{iaT_2} to obtain

$$0 = e^{iaT_2}\Bigg(\Big[\tfrac{1}{2}(T_3+T_1)-1-(T_3-T_1)\epsilon^{(0)}\Big]+\Big[(T_3-T_1)(H^{(1)}-\epsilon^{(1)}) + (T_3-T_1)(H^{(2)}-\epsilon^{(2)})+\cdots\Big]\Bigg)e^{-iaT_2}\Big(e^{iaT_2}R_{nl}\Big)$$
$$= \frac{\mathcal{N}}{n}\Bigg((T_3-n)+n\Big[n(T_3-T_1)(\tilde{H}^{(1)}-\epsilon^{(1)}+\tilde{H}^{(2)}-\epsilon^{(2)}+\cdots)\Big]\Bigg)\psi_{ql} \quad (71)$$

where

$$\tilde{H}^{(i)} = e^{iaT_2}H^{(i)}e^{-iaT_2}, \quad (72)$$

and the ψ_{ql} are expanded in terms of the zeroth-order eigenfunctions of T_3,

$$T_3\psi_{ql}^{(0)} = q\psi_{ql}^{(0)} = n\psi_{q=n,l}^{(0)}, \quad (73)$$

where now eq. (71) can be written as

$$\Big[(T_3-n)+(H_{\text{eff.}}^{(1)}-\epsilon_{\text{eff.}}^{(1)})+(H_{\text{eff.}}^{(2)}-\epsilon_{\text{eff.}}^{(2)})+\cdots\Big](\psi_{nl}^{(0)}+\psi_{nl}^{(1)}+\psi_{nl}^{(2)}++\cdots)=0. \quad (74)$$

Here,

$$H_{\text{eff.}}^{(i)} = n^2(T_3-T_1)\tilde{H}^{(i)}, \qquad \epsilon_{\text{eff.}}^{(i)} = n^2(T_3-T_1)\epsilon^{(i)}. \quad (75)$$

Straightforward generalization of Rayleigh–Schrödinger perturbation theory in terms of the zeroth-order eigenfunctions of T_3 (rather than $H^{(0)}$), now yields

$$(\psi_{nl}^{(0)}|\epsilon_{\text{eff.}}^{(1)}|\psi_{nl}^{(0)}) = n^3\epsilon_{nl}^{(1)} = (\psi_{nl}^{(0)}|H_{\text{eff.}}^{(1)}|\psi_{nl}^{(0)}), \quad (76)$$

$$\psi_{nl}^{(1)} = \sum_{q\neq n} c_{ql}^{(1)}\psi_{ql}^{(0)}, \qquad \text{with } c_{ql}^{(1)} = \frac{(\psi_{ql}^{(0)}|(H_{\text{eff.}}^{(1)}-\epsilon_{\text{eff.}}^{(1)})|\psi_{nl}^{(0)})}{(n-q)}, \quad (77)$$

and

$$(\psi_{nl}^{(0)}|\epsilon_{\text{eff.}}^{(2)}|\psi_{nl}^{(0)}) = n^3\epsilon_{nl}^{(2)} = (\psi_{nl}^{(0)}|H_{\text{eff.}}^{(2)}|\psi_{nl}^{(0)}) + \sum_{q\neq n}\frac{(\psi_{nl}^{(0)}|(H_{\text{eff.}}^{(1)}-\epsilon_{\text{eff.}}^{(1)})|\psi_{ql}^{(0)})(\psi_{ql}^{(0)}|(H_{\text{eff.}}^{(1)}-\epsilon_{\text{eff.}}^{(1)})|\psi_{nl}^{(0)})}{(n-q)}. \quad (78)$$

Once the number, $\epsilon_n^{(1)}$, has been calculated, the matrix elements of $\epsilon_{\text{eff.}}^{(1)}$ can be calculated, but this operator now has off-diagonal connections through the T_1 part of the operator $(T_3 - T_1)$.

For nonspherically symmetric perturbations, the results of eqs. (76) through (78) will still apply for the nondegenerate case, e.g., for the hydrogenic ground state, $n = 1$, or for axially symmetric perturbations for the special states with $l = (n-1)$ and $m = \pm(n-1)$, provided the $\psi_{ql}^{(0)}$ of eqs. (76)–(78) are replaced with the full stretched state, $\Psi_{nlm}^{(0)}$. In addition, the sums over $q \neq n$ will have to include sums over states with $l' \neq l$, and possibly $m' \neq m$. For the general degenerate states, it

is best to parallel the treatment of the degenerate case of Chapter 24 and first make a similarity transformation of the operator

$$\left[(T_3 - n) + (H^{(1)}_{\text{eff.}} - \epsilon^{(1)}_{\text{eff.}}) + \cdots\right]$$

via a unitary operator, $e^{i\lambda G}$, where now

$$\begin{aligned}
(n'l'm'|G|nlm) &= \frac{-i}{(n'-n)}(n'l'm'|H^{(1)}_{\text{eff.}} - \epsilon^{(1)}_{\text{eff.}}|nlm) \quad \text{for } n' \neq n, \\
(nlm|G|n'l'm') &= \frac{-i}{(n-n')}(nlm|H^{(1)}_{\text{eff.}} - \epsilon^{(1)}_{\text{eff.}}|n'l'm') \quad \text{for } n' \neq n, \\
(nl'm'|G|nlm) &= (nlm|G|nl'm') = 0; \quad \text{for all } l', m' \text{ if } n' = n. \qquad (79)
\end{aligned}$$

This process leads to a matrix in the n subspace that is the analog of eq. (12) of Chapter 24, if the $H^{(i)}$ there are replaced by $H^{(i)}_{\text{eff.}} - \epsilon^{(i)}_{\text{eff.}}$ and the $E^{(0)}_n$ and $E^{(0)}_{q\neq n}$ of Chapter 24 are now replaced by n and q. The pure numbers $\epsilon^{(1)}_n$ may first have to be determined by diagonalizing this matrix in first order in λ, but the $\epsilon^{(1)}_{\text{eff.}}$ contributes to the off-diagonal sums in second order through its $(T_3 - T_1)$ factor.

The greatest usefulness of the stretched spherical hydrogenic basis comes into play with spherically symmetric perturbations.

G An Application: Coulomb Potential with a Perturbing Linear Potential: Charmonium

A Coulomb potential with a linear confining potential may have some useful applications. The charmed quark-charmed antiquark two-body system has particles heavy enough so that nonrelativistic quantum theory may be a very good approximation. The bound states of this system have been described by an attractive $1/r$ color-electric potential augmented by a linear confining potential. For the deeply bound states, where the $1/r$ potential predominates, the linear (repulsive) confining potential may be treated as a perturbation. We then have a perturbed Coulomb problem with

$$H^{(1)} = V^{(1)}(r) = +\lambda r, \qquad H^{(2)} = 0, \qquad (80)$$

where we assume $\lambda \ll 1$ and r is again a dimensionless r. Also, $\lambda > 0$. Now,

$$H^{(1)}_{\text{eff.}} = \lambda n^3 (T_3 - T_1)^2, \qquad \epsilon^{(i)}_{\text{eff.}} = n^2 (T_3 - T_1)\epsilon^{(i)}_n. \qquad (81)$$

By rewriting

$$(T_3 - T_1) = T_3 - \tfrac{1}{2}(T_+ + T_-) \qquad \text{and} \qquad (82)$$

$$\begin{aligned}
(T_3 - T_1)^2 &= T_3^2 + \tfrac{1}{4}(T_+T_- + T_-T_+) - T_+(T_3 + \tfrac{1}{2}) - T_-(T_3 - \tfrac{1}{2}) \\
&\quad + \tfrac{1}{4}T_+T_+ + \tfrac{1}{4}T_-T_- \\
&= \tfrac{3}{2}T_3^2 - \tfrac{1}{2}l(l+1) - T_+(T_3 + \tfrac{1}{2}) - T_-(T_3 - \tfrac{1}{2}) \\
&\quad + \tfrac{1}{4}T_+T_+ + \tfrac{1}{4}T_-T_-, \qquad (83)
\end{aligned}$$

we can use the simple matrix elements of T_3, $T_\pm$ to obtain, via eq. (76),

$$\epsilon_n^{(1)} = \lambda\Big[\tfrac{3}{2}n^2 - \tfrac{1}{2}l(l+1)\Big], \tag{84}$$

and via eq. (78),

$$\begin{aligned} n^3\epsilon_n^{(2)} = & \\ & \frac{1}{(-1)}\left[\Big(-n^3\lambda(n+\tfrac{1}{2}) + \tfrac{1}{2}n^2\epsilon_n^{(1)}\Big)\sqrt{(n-l)(n+l+1)}\right]^2 \\ & + \frac{1}{(+1)}\left[\Big(-n^3\lambda(n-\tfrac{1}{2}) + \tfrac{1}{2}n^2\epsilon_n^{(1)}\Big)\sqrt{(n+l)(n-l-1)}\right]^2 \\ & + \frac{1}{(-2)}\left[\tfrac{1}{4}\lambda n^3\sqrt{(n+1-l)(n+2+l)(n-l)(n+1+l)}\right]^2 \\ & + \frac{1}{(+2)}\left[\tfrac{1}{4}\lambda n^3\sqrt{(n-1+l)(n-2-l)(n+l)(n-1-l)}\right]^2 \\ & = -\lambda^2\tfrac{1}{8}n^5\Big(7n^4 + 5n^2 - 3l^2(l+1)^2\Big), \end{aligned} \tag{85}$$

leading to

$$\epsilon = -\frac{1}{2n^2} + \lambda\Big[\tfrac{3}{2}n^2 - \tfrac{1}{2}l(l+1)\Big] - \lambda^2\tfrac{1}{8}n^2\Big[7n^4 + 5n^2 - 3l^2(l+1)^2\Big] + \cdots. \tag{86}$$

H Matrix Elements of the Vector Operators, $\vec{r}$ and $r\vec{p}$, in the Stretched Basis

In the last example, all of the needed matrix elements involved merely matrix elements of the SO(2,1) generators, T_i. For spherically nonsymmetric perturbations, however, we will encounter spherical tensors of higher rank that can change the quantum numbers l and m. The basic operators, from which more complicated ones can be built, are the vector operators, $\vec{r}$ and $\vec{p}$. So far, the only l step operators we have met are the components of the Runge–Lenz vector, which left the principal quantum number, n, invariant. Conversely, the ladder operators, $T_\pm$, of SO(2,1) could change only the n quantum number within a ladder of a definite l. The general vector operator, such as $\vec{r}$ and $\vec{p}$, can change both n and l.

Recall, first, the Runge–Lenz vector, in the form of the vector, $\vec{V}$, is given by

$$\begin{aligned} \vec{V} &= \frac{1}{\sqrt{(-2\epsilon)}}\left[\vec{r}\big(\tfrac{1}{2}(\vec{p}\cdot\vec{p})\big) - \vec{p}(\vec{r}\cdot\vec{p}) + \vec{r}\big[\tfrac{1}{2}(\vec{p}\cdot\vec{p}) - \frac{1}{r}\big]\right] \\ &= n\left[\vec{r}\big[\tfrac{1}{2}(\vec{p}\cdot\vec{p})\big] - \vec{p}(\vec{r}\cdot\vec{p}) + \vec{r}\Big(\frac{-1}{2n^2}\Big)\right], \end{aligned} \tag{87}$$

where this has been put into the most convenient form for conversion into its stretched counterpart, $\tilde{\vec{V}} \equiv \vec{A}$,

$$\tilde{\vec{V}} = e^{iaT_2}\vec{V}e^{-iaT_2} \equiv \vec{A} = n\Big[n\vec{r}\frac{(\vec{p}\cdot\vec{p})}{2n^2} - \frac{\vec{p}}{n}(n\vec{r}\cdot\frac{\vec{p}}{n}) + n\vec{r}\Big(\frac{-1}{2n^2}\Big)\Big]$$

$$\equiv \vec{A} = \vec{r}\left(\tfrac{1}{2}(\vec{p}\cdot\vec{p})\right) - \vec{p}(\vec{r}\cdot\vec{p}) - \tfrac{1}{2}\vec{r}. \tag{88}$$

Because

$$\begin{aligned}
&\int d\Omega \int_0^\infty dr r^2 (R_{nl'} Y_{l'm'})^* V_\mu R_{nl} Y_{lm} \\
&= \int d\Omega \int_0^\infty dr r \left(\frac{\psi_{nl'}}{n} Y_{l'm'}\right)^* \left(e^{iaT_2} r e^{-iaT_2}\right) \tilde{V}_\mu \frac{\psi_{nl}}{n} Y_{lm} \\
&= \int d\Omega \int_0^\infty dr r \left(\frac{\psi_{nl'}}{n} Y_{l'm'}\right)^* \left(n(T_3 - T_1)\right) \tilde{V}_\mu \frac{\psi_{nl}}{n} Y_{lm} \\
&= \int d\Omega \int_0^\infty dr r (\psi_{nl'} Y_{l'm'})^* \tilde{V}_\mu \psi_{nl} Y_{lm},
\end{aligned} \tag{89}$$

where we have used $T_3 \psi_{nl'} = n\psi_{nl'}$ and the fact that T_1 has no matrix elements diagonal in n,

$$\langle nl'm'|V_\mu|nlm\rangle = (nl'm'|A_\mu|nlm). \tag{90}$$

The reduced matrix elements of $\vec{A}$ in the stretched basis are therefore the same as the reduced matrix elements of $\vec{V}$ in the conventional basis.

$$\begin{aligned}
(n(l+1)\|\vec{A}\|nl) &= \sqrt{(l+1)[n^2 - (l+1)^2]} \\
(n(l-1)\|\vec{A}\|nl) &= -\sqrt{l[n^2 - l^2]} \\
(nl\|\vec{A}\|nl) &= 0.
\end{aligned} \tag{91}$$

In addition, the commutator algebra of the six operators $\vec{L}$ and $\vec{A}$ is the same as that of $\vec{L}$ and $\vec{V}$. Also, because $\vec{L}$ are functions only of θ, ϕ and $\partial/\partial\theta$, $\partial/\partial\phi$,

$$[T_2, L_j] = 0, \qquad \text{for } j = 1, 2, 3. \tag{92}$$

Finally,

$$\begin{aligned}
[T_2, A_j] &= [\frac{1}{i}\left(r\frac{\partial}{\partial r} + 1\right), \tfrac{1}{2}x_j\left((\vec{p}\cdot\vec{p}) - 1\right) - p_j(\vec{r}\cdot\vec{p})] \\
&= i\left(\tfrac{1}{2}x_j(\vec{p}\cdot\vec{p}) - p_j(\vec{r}\cdot\vec{p}) + \tfrac{1}{2}x_j\right) = iB_j,
\end{aligned} \tag{93}$$

where we have introduced the vector, $\vec{B}$, given by

$$\begin{aligned}
\vec{B} &= \left(\tfrac{1}{2}\vec{r}(\vec{p}\cdot\vec{p}) - \vec{p}(\vec{r}\cdot\vec{p}) + \tfrac{1}{2}\vec{r}\right), \\
\text{while} \quad \vec{A} &= \left(\tfrac{1}{2}\vec{r}(\vec{p}\cdot\vec{p}) - \vec{p}(\vec{r}\cdot\vec{p}) - \tfrac{1}{2}\vec{r}\right).
\end{aligned} \tag{94}$$

In particular,

$$\vec{r} = \vec{B} - \vec{A}, \tag{95}$$

and we have expressed the needed vector, $\vec{r}$, in terms of operators which make it convenient to calculate its matrix elements in the stretched hydrogenic basis. In particular, from the commutator

$$[T_2, A_3] = iB_3, \qquad \text{or} \quad B_3 = \tfrac{1}{2}[(T_- - T_+), A_3], \tag{96}$$

we get the matrix elements (in the stretched basis!),

$$\begin{aligned}(n'l'm|B_3|nlm) &= (n'l'\|\vec{B}\|nl)\frac{\langle lm10|l'm\rangle}{\sqrt{(2l'+1)}} \\ &= \tfrac{1}{2}\Big[(n'l'm|(T_- - T_+)|nl'm)(nl'\|\vec{A}\|nl) \\ &\quad - (n'l'\|\vec{A}\|n'l)(n'lm|(T_- - T_+)|nlm)\Big]\frac{\langle lm10|l'm\rangle}{\sqrt{(2l'+1)}}. \end{aligned} \tag{97}$$

$\vec{A}$ can change only $l \to (l \pm 1)$, but keeps n invariant, whereas $T_\pm$ changes only $n \to (n \pm 1)$ but keeps l invariant. The sum over intermediate states in the above relation has thus collapsed to a single term for each of the four possible $n'l'$ values of $(n \pm 1)(l \pm 1)$. In addition, because $\vec{r} = \vec{B} - \vec{A}$, and because the nonzero matrix elements of $\vec{A}$ are restricted to $n', l' = n, (l \pm 1)$, we can obtain the reduced matrix elements of $\vec{r}$ in the stretched basis by combining the above relation with the known matrix elements of $\vec{A}$ to yield

$$\begin{aligned}((n+1)(l+1)\|\vec{r}\|nl) &= +\tfrac{1}{2}\sqrt{(l+1)(n+l+1)(n+l+2)} \\ (n(l+1)\|\vec{r}\|nl) &= -\sqrt{(l+1)(n+l+1)(n-l-1))} \\ ((n-1)(l+1)\|\vec{r}\|nl) &= +\tfrac{1}{2}\sqrt{(l+1)(n-l-1)(n-l-2)} \\ ((n+1)(l-1)\|\vec{r}\|nl) &= -\tfrac{1}{2}\sqrt{l(n-l+1)(n-l)} \\ (n(l-1)\|\vec{r}\|nl) &= +\sqrt{l(n+l)(n-l)} \\ ((n-1)(l-1)\|\vec{r}\|nl) &= -\tfrac{1}{2}\sqrt{l(n+l-1)(n+l)}. \end{aligned} \tag{98}$$

Because $\vec{r}$ can be combined with itself or with functions of $r = (T_3 - T_1)$, we can use the above matrix elements to gain the matrix elements of more complicated functions of $\vec{r}$ and r. To get reduced matrix elements of $\vec{p}$, we note that

$$[T_3, B_3] = -irp_3. \tag{99}$$

This simple commutator can thus be used to generate matrix elements of a new vector,

$$r\vec{p} \equiv \vec{C}. \tag{100}$$

This relation is ideal for matrix elements in the stretched hydrogenic basis, because the needed vector $\vec{p}$ in the conventional basis will lead to matrix elements of $r\vec{p}$ in the stretched basis. The commutator relation $rp_3 = +i[T_3, B_3]$ leads at once to

$$\begin{aligned}(n'l'm|rp_3|nlm) &= +i(n'-n)(n'l'm|B_3|nlm), \\ (n'l'\|r\vec{p}\|nl) &= +i(n'-n)(n'l'\|\vec{B}\|nl). \end{aligned} \tag{101}$$

We have now met four vector operators, $\vec{L}$, $\vec{A}$, $\vec{B}$, $\vec{C}$, and the three components T_j. We have already seen $\vec{L}$ and $\vec{A}$ form the six components of a 4-D angular momentum algebra, if we identify $A_j = L_{j4}$. If we further identify $B_j = L_{j5}$, and

$C_j = L_{j6}$, and $T_2 = L_{45}$, $T_1 = L_{46}$, $T_3 = L_{56}$, so, with $j, k = 1, \ldots, 6$,

$$L_{jk} = \begin{pmatrix} 0 & L_3 & -L_2 & A_1 & B_1 & C_1 \\ -L_3 & 0 & L_1 & A_2 & B_2 & C_2 \\ L_2 & -L_1 & 0 & A_3 & B_3 & C_3 \\ -A_1 & -A_2 & -A_3 & 0 & T_2 & T_1 \\ -B_1 & -B_2 & -B_3 & -T_2 & 0 & T_3 \\ -C_1 & -C_2 & -C_3 & -T_1 & -T_3 & 0 \end{pmatrix}, \tag{102}$$

where the $L_{jk} = -L_{kj}$ are "angular momentum" operators in a (4+2)-dimensional space, with commutation relations

$$[L_{ab}, L_{ac}] = i g_{aa} L_{bc}, \qquad \text{with } g_{aa} = +1 \text{ for } a = 1, 2, 3, 4,$$

$$g_{55} = g_{66} = -1. \tag{103}$$

These 15 operators generate the group SO(4,2). We will not, however, need to make use of the detailed properties of this relatively complicated group! In order to solve hydrogenic perturbation problems, it will be sufficient for us to know the matrix elements of $\vec{L}$, including the m step operators $L_\pm$, of $\vec{A}$ that are the l step operators for a fixed n, of $T_\pm$ that are the n step operators for a fixed l, and, finally, of the vector operators $\vec{r} = \vec{B} - \vec{A}$, and $r\vec{p} = \vec{C}$. We have now achieved this goal.

I Second-Order Stark Effect of the Hydrogen Ground State Revisited

Let us now reexamine the second-order Stark effect in the ground state of the hydrogen atom by using the stretched hydrogenic basis. The perturbing Hamiltonian can be written as

$$H^{(1)} = -\lambda r \cos\theta, \tag{103}$$

where r is now dimensionless and $\lambda = (ea_0\mathcal{E})/(Ze^2/a_0)$ is also dimensionless. In the ground state with $n = 1, l = 0$, no diagonal matrix element exists, so $\epsilon^{(1)}_{n=1} = 0$. We therefore have $\epsilon^{(1)}_{\text{eff.}} = 0$, and, with $n = 1$,

$$H^{(1)}_{\text{eff.}} = -\lambda(T_3 - T_1)\vec{r}_0 = -\lambda(T_3 - \tfrac{1}{2}T_+ - \tfrac{1}{2}T_-)\vec{r}_0. \tag{104}$$

From our tabulation of reduced matrix elements of $\vec{r}$,

$$(n'10|\vec{r}_0|n = 1, l = 0, m = 0) = \frac{\langle 0010|10\rangle}{\sqrt{3}}(n'1\|\vec{r}\|10) = \frac{1}{\sqrt{3}}\delta_{n'2}\sqrt{\frac{3}{2}}. \tag{105}$$

Combining this with the matrix elements of T_3, $T_\pm$, we have

$$\begin{aligned}(210|H^{(1)}_{\text{eff.}}|100) &= -\lambda\sqrt{2}, \\ (310|H^{(1)}_{\text{eff.}}|100) &= +\lambda\sqrt{\frac{1}{2}}.\end{aligned} \tag{106}$$

The generalization of eq. (78) for the 3-D stretched basis then gives

$$\epsilon^{(2)} = -\lambda^2\Big[\frac{2}{(2-1)} + \frac{1}{2}\frac{1}{(3-1)}\Big] = -\lambda^2\frac{9}{4}, \tag{107}$$

in agreement with the result of eq. (7), but now from the simple addition of two terms (no infinite sums over a set of discrete states and no integrals over a continuum!).

J The Calculation of Off-Diagonal Matrix Elements via the Stretched Hydrogenic Basis

We have seen how use of the stretched basis greatly simplifies calculations for a specific bound state. The stretched hydrogenic basis may also be used to simplify off-diagonal matrix elements for transitions between different bound states. An example is the electric dipole moment matrix element between different hydrogen bound states. In eq. (4), we used the matrix element of $r\cos\theta$ between a p-state of arbitrary n and the ground state. This process requires the calculation of the conventional matrix element

$$\langle 100|r\cos\theta|n10\rangle = \frac{1}{\sqrt{3}}\int_0^\infty drr^3 R^*_{n=1,l=0}(r)R_{n,l=1}(r).$$

Let us transcribe this equation into the stretched basis for the state with arbitrary n, via

$$\begin{aligned}
&\int_0^\infty drr^3 R^*_{n=1,l=0}(r)R_{n,l=1}(r)\\
&= \int_0^\infty drr\Big(e^{iaT_2}R_{10}(r)\Big)^*(e^{iaT_2}r^2e^{-iaT_2})\Big(e^{iaT_2}R_{n1}(r)\Big)\\
&= \int_0^\infty drr\Big(e^{iaT_2}R_{10}(r)\Big)^* n^2r^2\frac{1}{n}\psi_{q=n,l=1}\\
&= \int_0^\infty drr\Big(n2e^{-nr}\Big)^* nr^2\frac{2^2}{\sqrt{(n+1)!(n-2)!}}\frac{e^r}{r^2}\frac{d^{n-2}}{dr^{n-2}}\Big(r^{n+1}e^{-2r}\Big),
\end{aligned} \tag{109}$$

where, with $e^a = n$, we have used, see eq. (36),

$$e^{iaT_2}R_{10}(r) = e^aR_{10}(e^ar) = nR_{10}(nr),$$

for the 1s state of the left-hand side, and have substituted the general derivative expression for the stretched state, $\psi_{n,1}(r)$, derived in eq. (66). We therefore have

$$\begin{aligned}
&\langle 100|r\cos\theta|n10\rangle =\\
&\frac{2^3n^2}{(n-2)!\sqrt{3(n+1)n(n-1)}}\int_0^\infty drre^{-(n-1)r}\frac{d^{n-2}}{dr^{n-2}}\Big(r^{n+1}e^{-2r}\Big).
\end{aligned} \tag{110}$$

The last integral is performed by integrating by parts $(n-2)$ times to yield

$$\int_0^\infty drre^{-(n-1)r}\frac{d^{n-2}}{dr^{n-2}}\Big(r^{n+1}e^{-2r}\Big) = \int_0^\infty dr(n-1)^{n-2}r^{n+2}e^{-(n+1)r}$$

$$-(n-2)\int_0^\infty dr(n-1)^{n-3}r^{n+1}e^{-(n+1)r} = \frac{(n-1)^{n-3}}{(n+1)^{n+3}}(n+1)!2n, \quad (111)$$

leading to the final result

$$\langle 100|r\cos\theta|nl=10\rangle = \frac{(n-1)^{n-3}}{(n+1)^{n+3}}2^4n^3\sqrt{\frac{(n+1)n(n-1)}{3}}. \quad (112)$$

K Final Remarks

As we have seen, the techniques introduced in this chapter are particularly useful for spherically symmetric perturbations of the hydrogenic atom. For nonspherically symmetric perturbations, the stretched hydrogenic basis can be used to get second-order results, but the solution for the final eigenvalues and eigenvectors still requires the diagonalization of some finite-dimensional matrices. For axially symmetric perturbations, parabolic coordinates are more convenient. We have seen in problem 26 that stretched parabolic coordinates, μ, ν, can be expressed in term of two commuting SO(2,1) groups with generators, T_i and T_i'. The zeroth-order hydrogen problem is then transformed into an eigenvalue equation of the form

$$(T_3+T_3')\psi_{n_1,m}(\mu)\psi_{n_2,m}(\nu)e^{\pm im\phi}$$
$$=\left[\left(\tfrac{1}{2}(m+1)+n_1\right)+\left(\tfrac{1}{2}(m+1)+n_2\right)\right]\psi_{n_1,m}(\mu)\psi_{n_2,m}(\nu)e^{\pm im\phi}, \quad (113)$$

with $(n_1+n_2+m+1)=n$, where n is the usual principal quantum number. The Stark effect has been solved to second order for arbitrary, n, using this $SO(2,1)\times SO(2,1)$ basis in problem 38.

A very good reference for the use of the stretched spherical basis for hydrogenic perturbation problems is: *Lie Algebraic Methods and their Applications to Simple Quantum Systems*; B. G. Adams, J. Cizek and J. Paldus, Advances in Quantum Chemistry **19** (1988) 1; and Barry G. Adams, *Algebraic Approach to Simple Quantum Systems*, New York: Springer-Verlag, 1994. For a detailed use of the stretched parabolic coordinates, see D. Delande and J. C. Gay, J. Phys. B: At. Mol. Phys. **17** (1984) L335.

Problems

48. Use the stretched spherical basis to show the conventional diagonal matrix element of r^2 is given by

$$\langle nlm|r^2|nlm\rangle = \tfrac{5}{2}n^4 - \tfrac{3}{2}n^2l(l+1) + \tfrac{1}{2}n^2.$$

49. Assume the attractive Coulombic $(1/r)$ potential for a two-body nonrelativistic system is perturbed by a quadratic repulsive term, with $H^{(1)} = +\lambda r^2$, where $\lambda \ll 1$ and r is dimensionless. Show that the energy through second order

is given by

$$\epsilon = -\frac{1}{2n^2} + \lambda\left(\tfrac{5}{2}n^4 - \tfrac{3}{2}n^2 l(l+1) + \tfrac{1}{2}n^2\right)$$

$$-\lambda^2 \frac{n^6}{16}\left(143n^4 + 345n^2 + 28 - 90n^2 l(l+1) - 21l^2(l+1)^2 - 126l(l+1)\right).$$

50. Use the stretched hydrogenic functions to show the conventional matrix element of the electric dipole moment between the $2s$ state and an arbitrary p state is given by

$$\langle 200|r\cos\theta|n10\rangle == \sqrt{\frac{(n+1)n(n-1)}{2\cdot 3}}\frac{2^9 n^3 (n-2)^{n-3}}{(n+2)^{n+3}}.$$

51. Write the dilation operator, $e^{iaT_2} = e^{\frac{1}{2}a(T_+ - T_-)}$, in its "disentangled" forms. In particular, show that

$$e^{iaT_2} = e^{-\tanh\frac{a}{2}T_-}(\cosh^2\tfrac{a}{2})^{T_0} e^{+\tanh\frac{a}{2}T_-},$$

$$e^{iaT_2} = e^{+\tanh\frac{a}{2}T_+}\frac{1}{(\cosh^2\frac{a}{2})^{T_0}} e^{-\tanh\frac{a}{2}T_-}.$$

Hint: Use (1) the corresponding result for the angular momentum operators of SO(3) (see Chapter 29); (2) the fact that the operators T_3, iT_+, iT_- of SO(2,1) have formally the same commutation relations as the operators J_3, J_+, J_- of SO(3); and (3) the fact that the disentanglement relations depend only on the commutator algebra of the operators. Use these relations to rederive the result of eq. (112), without the use of the explicit functional forms of the radial functions, by relating the conventional matrix element $\langle n10|r\cos\theta|100\rangle$ to its stretched form

$$\langle n10|r\cos\theta|100\rangle = \frac{1}{n}(\Psi_{n10}|e^{iaT_2} r(\vec{r})_0|\Psi_{100})$$

$$= \frac{1}{n\sqrt{2}}(\Psi_{n10}|e^{+\frac{(n-1)}{(n+1)}T_+}\left[\frac{4n}{(n+1)^2}\right]^{T_3} e^{-\frac{(n-1)}{(n+1)}T_-}\left(T_3 - \tfrac{1}{2}(T_+ + T_-)\right)|\Psi_{210}),$$

where we have used $\vec{r}_0|\Psi_{100}) = \frac{1}{\sqrt{2}}|\Psi_{210}$), and $\tanh\frac{a}{2} = (n-1)/(n+1)$, $\cosh^2\frac{a}{2} = (n+1)^2/4n$.