Rydberg electron in a multipole field

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The states of a highly excited electron in a field of multipoles must be investigated in a number of problems of atomic physics. We develop here, for an analytic perturbation-theory calculation of quantum defects of Rydberg series, a procedure applicable in principle for arbitrary order of perturbation theory and for arbitrary multipole order. The calculations make use of the properties of the Coulomb problem at zero energy. The presence of a non-Coulomb central potential is taken into account with the aid of the model-potential method. The results are presented in the form of equivalent operators that describe the contribution of a given perturbation-theory order. Actual calculations are performed for dipole and quadrupole potentials in first and second order of perturbation theory.

1. INTRODUCTION

The problem of a highly excited electron in the field of multipoles is encountered in the theory of Rydberg states of molecules (see Ref. 1 and the bibliography therein). Similar problems can be encountered also in investigations of various centers in a crystal lattice. For doubly excited states of the helium atom, the multipole dynamic field acting on an external electron is produced by an internal electron.[2] An effective multipole potential appears also in the description of a hydrogen atom in the field of a high-frequency electromagnetic wave.[3]

The current literature contains detailed discussions of electron states in the field of a dipole (both pointlike and finite)—see, e.g., Ref. 4. This state is special, since it permits separation of the dynamic variables.

The variables do not separate for a multipole of arbitrary order, so that the problem is essentially three-dimensional. It is natural to investigate it by perturbation theory. Generally speaking, first-order perturbation theory in the multipole potential will not do here. For a dipole potential, for example, all the matrix elements in the subspace of states with a given principal quantum number vanish (details follow). We know that to calculate higher perturbation-theory orders it is necessary to sum over the entire energy spectrum of the quantum system, something analytically possible only in rare cases.

We show below that the problem of Rydberg states of an electron in a field of multipoles is unique in that in principle it can be analytically calculated for a multipole of any order, and in any order of perturbation theory. The calculation procedure is in fact the main result of the present paper, which can be used later in the diverse applications indicated above. It is based on special properties of the quantum-mechanical Coulomb problem at low energy.

In Sec. 2 we introduce the notation and formulate the approximation. It is expedient to present the results in the form of equivalent operators whose matrix elements on unperturbed states yield the energy corrections in the required order of perturbation theory. The equivalent operators themselves take the form of multipole potentials. Thus, for the contribution of a dipole perturbation in second-order perturbation theory such an operator is written in the form of a sum of a monopole and a quadrupole effective potentials. The presence of a central non-Coulomb potential is taken into account in the context of the well-known model-potential method.[5] As an example of the application of the proposed calculation procedure, we consider dipole and quadrupole interactions in first (Sec. 3) and second (Sec. 4) orders of perturbation theory.

2. PERTURBATION THEORY AT ZERO ENERGY

A central potential is applied to the unperturbed Hamiltonian of a Rydberg electron. In the simplest case we have a pure Coulomb interaction:

$$H_0=-\frac{1}{2}\nabla^2-\frac{1}{r}; \qquad (2.1)$$

here **r** is the radius vector of the electron, and we use the atomic system of units. The unperturbed wave function is

$$\psi^{(0)}_{nlm}(\mathbf{r})=R^{(0)}_{nl}(r)\,Y_{lm}(\mathbf{N}),\qquad \mathbf{N}=\mathbf{r}/r, \qquad (2.2)$$

where l and m are the usual spherical quantum numbers. For the radial wave function at low energy E we use the well known approximate expression[6]

$$R^{(0)}_{nl}(r)=\frac{2^{1/2}}{n^{3/2}}\frac{1}{r^{1/2}}J_{2l+1}[(8r)^{1/2}], \qquad (2.3)$$

which is valid under the condition $r\ll|E|^{-1}$.

The unperturbed Hamiltonian has a simple generalization that makes it possible to take into account the difference between a central and a Coulomb potential. To this end, a model potential is introduced into the Hamiltonian (see, e.g., Ref. 5)

$$H_0=-\frac{1}{2}\nabla^2-\frac{1}{r}+\sum_l\frac{c_l}{r^2}P_l, \qquad (2.4)$$

where P_l is the operator of projection on a subspace of states with a given orbital quantum number l; the constants c_l designate the potential power at a given l. The electron radial motion in such a potential is characterized by an effective orbital momentum λ_l:

$$\lambda_l=[(l+{}^1/_2)^2+2c_l]^{1/2}-{}^1/_2. \qquad (2.5)$$

The radial wave function is

$$R^{(0)}_{nl}(r)=\frac{2^{1/2}}{n^{3/2}}\frac{1}{r^{1/2}}J_{2\lambda_l+1}[(8r)^{1/2}]. \qquad (2.6)$$

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Another more universal possibility of taking into account the short-range non-Coulomb interaction of the Rydberg electron and the atomic core is connected with R-matrix theory (see, e.g., Ref. 7). In this theory the wave function outside the core (i.e., in the range of action of the pure Coulomb potential), at $r \ll |E|^{-1}$, is a superposition of Bessel and Neumann functions:

$$R_{nl}^{(0)}(r) = \frac{2^{1/2}}{n^{3/2}} \frac{1}{r^{1/2}} (\alpha^2+1)^{-1/2} \{\alpha J_{2l+1}[(8r)^{1/2}] + N_{2l+1}[(8r)^{1/2}]\}. \tag{2.7}$$

If the parameter is properly chosen $\alpha = \cot[(\pi/2)(1-\lambda_l])$ this function has in the semiclassical region an asymptote that coincides with the asymptotic function (1.6); this serves as an additional corroboration of the model-potential method. In principle, our calculation method can be developed also using R-matrix theory. However, since the function (2.7) does not decrease as $r \to 0$, it is necessary to trace in the calculations the contribution of the region of small r to the matrix elements. The actual equations that can be obtained in this case require therefore a separate analysis and will not be discussed here.

In both cases the energy levels make up a Rydberg series

$$E_{nl} = -\frac{1}{2(n+\delta_l)^2}, \tag{2.8}$$

where δ_l is the quantum defect ($\delta_l = \lambda_l - l$).

The role of the perturbation is assumed by the sum of the electric-multipole potentials

$$V(\mathbf{r}) = \sum_k (A_k V_k) \equiv \sum_{k\varkappa} A_{k\varkappa} V_{k\varkappa}, \tag{2.9}$$

where k is the order of the multipole ($k = 1,2,3,4...$, for a dipole, quadrupole, octupole, hexadecapole, etc.),

$$V_{k\varkappa}(\mathbf{r}) = v_k(r) Y_{k\varkappa}(\mathbf{N}). \tag{2.10}$$

For an electric multipole, the potential has a power-law radial dependence:

$$v_k(r) = r^{-k-1}, \tag{2.11}$$

so that the function $V_{k\varkappa}(\mathbf{r})$ (2.10) is harmonic (satisfies the Laplace equation $\nabla^2 V_{k\varkappa} = 0$ at all points except the origin). The irreducible spherical tensor $A_{k\varkappa}$ indicates the orientation of the perturbation potential (for $k = 1$, for example, the direction of the vector of the corresponding dipole moment).

The corrections to the energy level are given by the usual Rayleigh–Schrödinger perturbation-theory equations

$$\delta E = \langle \psi_{nlm} | V | \psi_{nlm} \rangle + \langle \psi_{nlm} | V \tilde{G}(E_{nl}) V | \psi_{nlm} \rangle + \ldots, \tag{2.12}$$

where $G(E)$ is the Green's function, and the tilde labels reduced functions.

The kernel of the operator $G(E)$ is represented in the usual fashion by an expansion in partial waves:

$$G(\mathbf{r}_1, \mathbf{r}_2, E) = \sum_{l_2 m_2} Y^*_{l_2 m_2}(\mathbf{N}_1) Y_{l_2 m_2}(\mathbf{N}_2) g_{l_2}(r_1, r_2), \tag{2.13}$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_1} + \sum_{l_1} \frac{c_{l_1}}{r_1^2} P_{l_1} - E\right) G(\mathbf{r}_1, \mathbf{r}_2, E) = \delta(\mathbf{r}_1 - \mathbf{r}_2). \tag{2.14}$$

The radial Green's function $g_l(r_1, r_2)$ is constructed in the usual manner from solutions of the unperturbed radial equation at a given l, one regular as $r \to 0$ (F_l) and other decreasing as $r \to \infty$ (G_l):

$$g_l(r_1, r_2) = \frac{1}{W} F_l(r_<) G_l(r_>), \tag{2.15}$$

where $r_< = \min(r_1, r_2)$, $r_> = \max(r_1, r_2)$ and W is the Wronskian of the solutions of F_l and G_l. Within the framework of the method of the model potential, F_l is given by expression (2.6). Outside the core, at $r \ll |E|^{-1}$, the function G_l takes the form (see Appendix 1):

$$G_l(r) = r^{-1/2} \{J_{2\lambda_l+1}[(8r)^{1/2}] \operatorname{ctg} \varphi_l(E) + N_{2\lambda_l+1}[(8r)]^{1/2}\}, \tag{2.16}$$

$$\varphi_l(E) = \pi[(-2E)^{-1/2} - \lambda_l].$$

The spectrum of the problem is specified by the condition $\varphi_l(E) = \pi n$, which leads to (2.8). To change to the reduced Green's function it is necessary to separate the pole term at $E = E_{nl}$, which results in

$$\tilde{G}_l(r) = r^{-1/2} \{J_{2\lambda_l+1}[(8r)^{1/2}] 3[\pi(n+\delta_l)]^{-1} + N_{2\lambda_l+1}[(8r)^{1/2}]\}. \tag{2.17}$$

Ultimately, in the principal order as $n \to \infty$, we get

$$\tilde{g}_l(r_1, r_2) = -\frac{2\pi}{(r_1 r_2)^{1/2}} J_{2\lambda_l+1}[(8r_<)^{1/2}] N_{2\lambda_l+1}[(8r_>)^{1/2}]. \tag{2.18}$$

3. EQUIVALENT OPERATORS. GENERAL RESULTS

Let us consider in greater detail the calculation of the second-order perturbation-theory correction. Since the perturbation (2.9) is a sum of multipole potentials, it is necessary in the general case to calculate the correction of a mixed perturbation theory with potentials of multipoles of order k_1 and k_2

$$\langle \psi_{nl_1m_1} | (A_{k_1} V_{k_1}) \tilde{G}(E_{nl_2}) (A_{k_2} V_{k_2}) | \psi_{nl_3m_3} \rangle. \tag{3.1}$$

We consider here an off-diagonal (in l and m) composite matrix element taken between the states $\psi_{nl_1m_1}$ and $\psi_{nl_3m_3}$. The latter, generally speaking, is necessary since the unperturbed state (2.2) is degenerate in the azimuthal quantum number m, and in the case of a pure Coulomb unperturbed Hamiltonian also in the orbital number l. If the degeneracy is not lifted (at least partially) in first-order perturbation theory, it is well known[8] that in second order it is necessary to diagonalize the matrix $V\tilde{G}V$.

Using the expansion (2.13) and the formalism of angular-momentum theory[9] we can represent (3.1) by a matrix element (in the angle variables) of a certain effective operator $W(k_1, k_2, l_1, l_3)$:

$$\langle \psi_{nl_1m_1} | (A_{k_1} V_{k_1}) \tilde{G}(E_{nl_2}) (A_{k_2} V_{k_2}) | \psi_{nl_3m_3} \rangle$$
$$= \langle Y_{l_1m_1} | W(k_1, k_2, l_1, l_3) | Y_{l_3m_3} \rangle, \tag{3.2}$$

in the form of an expansion in the multipoles q:

$$W = \sum_q (\mathscr{A}_q W_q), \qquad \mathscr{A}_q = (A_{k_1} \otimes A_{k_2})_q. \tag{3.3}$$

We use here the standard notation for a tensor product of irreducible operators[9]:

$$(A_{J_1}\otimes B_{J_2})_{JM}=\sum_{M_1M_2} C^{JM}_{J_1M_1J_2M_2} A_{J_1M_1} B_{J_2M_2}, \tag{3.4}$$

$$(A_J B_J)=\sum_M A_{JM} B_{JM}, \tag{3.5}$$

where $C^{JM}_{J_1M_1J_2M_2}$ are Clebsch–Gordan coefficients. The operator $W_{q\xi}$ is an irreducible spherical tensor, and its matrix elements in the angle variables are expressed in terms of the irreducible matrix element $\langle l_1\| W_q \|l_3\rangle$:

$$\langle Y_{l_1m_1}| W_{q\xi} | Y_{l_3m_3}\rangle=(-1)^{2q} C^{l_1m_1}_{l_3m_3q\xi} \frac{\langle l_1\| W_q\| l_3\rangle}{(2l_1+1)^{1/2}}. \tag{3.6}$$

For the latter we obtain the expression

$$\langle l_1 | W_q | l_3\rangle=\sum_{l_2} \langle l_1 \| w_q^{(l_2)} \| l_3\rangle (R_{nl_1} | v_{k_1}\tilde{g}_{l_2} v_{k_2} | R_{nl_3}), \tag{3.7}$$

where

$$\langle l_1 \| w_q^{(l_2)} \| l_3\rangle$$
$$=\frac{(2l_2+1)}{4\pi}[(2l_1+1)(2l_3+1)(2k_1+1)(2k_2+1)(2q+1)]^{1/2}$$
$$\times\begin{pmatrix} l_1 & k_1 & l_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_2 & k_2 & l_3\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} k_1 & k_2 & q\\ l_3 & l_1 & l_2\end{Bmatrix}(-1)^{l_2+l_3+q}, \tag{3.8}$$

while

$$\begin{pmatrix} j_1 & j_2 & j_3\\ 0 & 0 & 0\end{pmatrix},\quad \begin{Bmatrix} a & b & c\\ d & e & f\end{Bmatrix}$$

are respectively $3jm$ and $6j$ symbols, and we have used the following abbreviated notation for the radial matrix element:

$$(R_{nl_1} | \hat{V} | R_{nl_3})=\int_0^\infty R_{nl_1}(r) \hat{V} R_{nl_3}(r) r^2\, dr. \tag{3.9}$$

Although (3.2)–(3.8) may seem unwieldy, their physical meaning is quite clear. The equivalent operator W is represented by a sum of multipoles whose order q, in accordance with the rule for angular-momentum addition, runs through values from $|k_1-k_2|$ to k_1+k_2 (the parity of q is the same as the parity of the sum k_1+k_2). The orientation of the qth multipole is characterized by an irreducible tensor $A_{q\xi}=(A_{k_1}\otimes A_{k_2})_{q\xi}$. In this respect (3.3) is quite analogous to Eq. (2.9) for the initial perturbation potential. An irreducible matrix element of the qth multipole is expressed as a sum over those values of the intermediate orbital momentum l_2 which are allowed by the angular-momentum-addition rules. The sum contains composite radial matrix elements, and their coefficients $\langle l_1 \| w_q^{(l_2)} \| l_3\rangle$ reflect the result of addition of the available angular momenta.

Since the principal quantum number n enters in the radial wave functions R_{nl_1} and R_{nl_3}, the corrections to the energy are of the same order in n (namely, $\sim n^{-3}$) for all multipoles and for an arbitrary order of perturbation theory. Comparing this circumstance with expression (2.8) for the energy of the Rydberg level, we see that the developed perturbation theory yields the quantum defect δ_l of the series, which is independent of n.

The results of the present section do not depend on the form of the function $v_k(r)$. The actual form of this function is needed for the calculation of the radial matrix elements.

4. FIRST-ORDER PERTURBATION THEORY

A methodologically important advantage of the approach developed in the present paper is the possibility of analytic calculation of the resultant radial matrix elements in all orders of perturbation theory. An important role is played here by the power-law dependence of the radial part $v_k(r)$ (2.11) of the perturbation. We begin the calculations with first-order perturbation theory.

The integral obtained for the dipole potential reduces to a tabulated one [Ref. 10, Eq. (7.14.32)], which yields

$$(R_{nl_1}|r^{-2}|R_{nl_3})=\frac{2}{\pi n^3}\frac{\sin[(\lambda_{l_1}-\lambda_{l_3})\pi]}{(\lambda_{l_1}-\lambda_{l_3})(\lambda_{l_1}+\lambda_{l_3}+1)}. \tag{4.1}$$

For a pure Coulomb central potential ($c_l\equiv 0$, $\lambda_{l_i}=l_i$) the integration over the angles in the matrix element yields $l_1-l_2=\pm 1$, and in this case the radial integral (4.1) vanishes. All the matrix elements of the dipole-potential operator are thus zero in the subspace of states with a given principal quantum number n. This property is preserved also for the exact Coulomb wave functions[11] (see also Ref. 2).

For a quadrupole potential, using the known recurrence relation for Bessel functions[10]

$$J_\nu(z)/z=\frac{1}{2\nu}(J_{\nu-1}(z)+J_{\nu+1}(z)), \tag{4.2}$$

we get

$$(R_{nl_1}|r^{-3}|R_{nl_3})$$
$$=\frac{8\sin[(\lambda_{l_1}-\lambda_{l_3})\pi]}{\pi n^3(2\lambda_{l_1}+1)(2\lambda_{l_3}+1)}\left\{\frac{\lambda_{l_1}+\lambda_{l_3}+1}{(\lambda_{l_1}-\lambda_{l_3})[(\lambda_{l_1}+\lambda_{l_3}+1)^2-1]}\right.$$
$$\left.-\frac{\lambda_{l_1}-\lambda_{l_3}}{(\lambda_{l_1}+\lambda_{l_3}+1)[(\lambda_{l_1}-\lambda_{l_3})^2-1]}\right\}. \tag{4.3}$$

This relation can be used, in particular, to take into account the influence of the quadrupole moment of the atomic nucleus on the Rydberg series of the levels. In the Coulomb case, in accordance with the results of Ref. 11, only the diagonal ($l_1=l_3$) matrix element differs from zero, and the result for this element coincides with the exact one[6]:

$$(R_{nl}|r^{-3}|R_{nl})=\frac{2}{n^3}\frac{1}{l(l+1)(2l+1)}. \tag{4.4}$$

5. SECOND-ORDER PERTURBATION THEORY

Dipole interaction

We consider first the calculation of the correction functions $R^{(1)}=g_{l_2}v_{k_2}|R_{nl_3})$ for first-order perturbation theory. The integrals obtained for finite-limit Bessel functions by using expressions (2.6) and (2.18) can be explicitly calculated and yield fairly compact results. Thus, in the dipole case ($k_2=1$) we obtain

$$R^{(1)}(r)=\frac{2^{3/2}r^{-1/2}}{n^{3/2}(\lambda_{l_2}-\lambda_{l_3})(\lambda_{l_2}+\lambda_{l_3}+1)}$$
$$\times\{J_{2\lambda_{l_3}+1}[(8r)^{1/2}]-\cos[\pi(\lambda_3-\lambda_2)]J_{2\lambda_{l_2}+1}[(8r)^{1/2}]\}. \tag{5.1}$$

For higher-order multipoles ($k_2>1$) it is necessary in addition to use the recurrence relation (4.2), and the correction function takes the form of a linear combination of Bessel functions with indices that differ by unity. Clearly, the application of the operator $q_{l_2'}v_{k_2'}$ to this function again leads to functions of the same type. This method makes it possible to obtain analytically a correction function of any perturbation-theory order for a multipole of arbitrary order.

We know that, given $\psi^{(1)}$ we can find, by taking the average of the perturbation at a distance $\psi^{(0)}+\psi^{(1)}$, the correction to the energy up to third order inclusive. We confine ourselves here to corrections up to second order, which are calculated with the aid of the equation

$$(R_{nl_1}|r^{-2}g_{l_2}r^{-2}|R_{nl_3})$$
$$=\frac{2}{\pi n^3}\frac{1}{(\lambda_{l_2}-\lambda_{l_3})(\lambda_{l_1}-\lambda_{l_2})(\lambda_{l_1}+\lambda_{l_2}+1)(\lambda_{l_2}+\lambda_{l_3}+1)}$$
$$\times\left\{\frac{(2\lambda_{l_1}+1)^2+(2\lambda_{l_3}+1)^2-2(2\lambda_{l_2}+1)^2}{4(\lambda_{l_1}-\lambda_{l_3})(\lambda_{l_1}+\lambda_{l_3}+1)}\sin[\pi(\lambda_{l_1}-\lambda_{l_3})]\right.$$
$$\left.-\sin[\pi(\lambda_{l_1}+\lambda_{l_3}-2\lambda_{l_2})]\right\}. \tag{5.2}$$

The result is particularly simple in the Coulomb case:

$$(R_{nl_1}|r^{-2}g_{l_2}r^{-2}|R_{nl_1})=\frac{2}{n^3}\frac{1}{(l_1+l_2+1)(2l_1+1)(l_1-l_2)}. \tag{5.3}$$

The effective operator W contains monopole ($q=0$) and quadrupole ($q=2$) terms. Direct calculation of (3.7) and (3.8) yields

$$\langle l\|W_0\|l\rangle=-\frac{1}{4\pi}\left(\frac{3}{2l+1}\right)^{1/2}\{(l+1)(R_{nl}|r^{-2}g_{l+1}r^{-2}|R_{nl})$$
$$+l(R_{nl}|r^{-2}g_{l-1}r^{-2}|R_{nl})\}, \tag{5.4}$$
$$\langle l\|W_2\|l\rangle=-\frac{1}{4\pi}\left(\frac{6l(l+1)}{(2l-1)(2l+1)(2l+3)}\right)^{1/2}$$
$$\times\{(2l-1)(R_{nl}|r^{-2}g_{l+1}r^{-2}|R_{nl})$$
$$+(2l+3)(R_{nl}|r^{-2}g_{l-1}r^{-2}|R_{nl})\} \tag{5.5}$$
$$\langle l+2\|W_2\|l\rangle=\frac{3}{4\pi}\left(\frac{l(l+2)}{2(2l+3)}\right)^{1/2}(R_{nl+2}|r^{-2}g_{l+1}r^{-2}|R_{nl}). \tag{5.6}$$

In the Coulomb case the results are greatly simplified:

$$\langle l\|W_0\|l\rangle=\langle l+2\|W_2\|l\rangle=0,$$
$$\langle l\|W_2\|l\rangle=\frac{8\pi}{6^{1/2}n^3}[(2l-1)(2l+1)(2l+3)l(l+1)]^{1/2}, \tag{5.7}$$

and correspond to the equivalence, established in Ref. 2, within the limits of the n layer (i.e., for all possible values of l_1 and l_3) of the following operators:

$$\frac{\mathbf{Ar}_1}{r_1^3}G(E_n)\frac{\mathbf{Br}_1}{r_1^3},\quad\frac{3(\mathbf{Ar}_1)(\mathbf{Br}_1)-(\mathbf{AB})r_1^2}{2r_1^5} \tag{5.8}$$

for arbitrary constant vectors **A** and **B**. Note that the algebraic method used to establish the equivalence of the operators (5.8) cannot be used in the case of the unperturbed Hamiltonian (2.4).

6. SECOND-ORDER PERTURBATION THEORY. GENERAL CASE

To write down in compact form the second-order perturbation-theory correction in the case of a perturbation of arbitrary multipolarity, we note that with the aid of (2.6) and (4.2) one can write

$$\frac{1}{r}R_{nl}(r)=(\hat{D})^2R_{nl}(r). \tag{6.1}$$

The operator $\hat{D}$ acts here on the orbital quantum number l and can be formally written in the form

$$\hat{D}\Phi_l=\frac{1}{2^{1/2}(l+{}^1/_2)}(\Phi_{l-1}+\Phi_{l+1}). \tag{6.2}$$

The composite second-order matrix element then takes the form

$$(R_{nl_1}|r^{-k_1-1}g_{l_2}r^{-k_2-1}|R_{nl_3})=\sum_{l_1',l_3'}[(\hat{D})^{2(k_1-1)}]_{l_1l_1'}$$
$$\times[(\hat{D})^{2(k_2-1)}]_{l_3l_3'}(R_{nl_1'}|r^{-2}g_{l_2}r^{-2}|R_{nl_3'}), \tag{6.3}$$

and yields, in conjunction with (5.2), an analytic expression for any multipolarity. It is possible quite analogously, to express also the matrix elements containing an arbitrary number of Green's functions, i.e., corresponding to any order of perturbation theory.

By way of example, Appendix 2 shows the calculation results for quadrupole interaction in second-order perturbation theory.

7. CONCLUSION

We have described here a procedure of calculating high perturbation-theory orders in the case of noncentral potentials of a special type, viz., fields of electric quadrupoles. We have used essentially the smallness of the unperturbed-state energy, and also the power-law dependence of the perturbation on the radial coordinate. Analytic results have been obtained also for an arbitrary integer exponent that is not connected with the index of the spherical function in expression (2.10). For electric-multipole potentials there exist many useful algebraic relations that generalize the statement that the operators (5.8) are equivalent; these relations must be considered separately.

We conclude by pointing to a probable connection between our present results and the special symmetry properties of the Coulomb problem at zero energy, properties described by a motion group of three-dimensional Euclidean space.

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APPENDIX 1

The function G_l is by definition a solution of an unperturbed radial equation that decreases exponentially as $r\to\infty$. In the region of classically allowed motion outside the core, the semiclassical expression for this function takes the form[8]

$$G_l(r)=r^{-1}p^{-1/2}\cos\left(\int_r^{r_{max}}p(r)\,dr-\frac{\pi}{4}\right),$$
$$p(r)=\left\{2\left[E+\frac{1}{r}-\frac{(\lambda_l+{}^1/_2)^2}{2r^2}\right]\right\}^{1/2}, \tag{A1.1}$$

with $r_{\max}$ and $r_{\min}$ respectively the right- and left-hand turning points for the radial motion. The integral in this expression is easily evaluated:

$$\int_r^{r_{max}}p\,dr=\int_{r_{min}}^{r_{max}}p\,dr-\int_{r_{min}}^{r}p\,dr=\frac{\pi}{(-2E)^{1/2}}-(8r)^{1/2}, \tag{A1.2}$$

where the second integral is calculated under the assumption that $r \ll |E|^{-1}$. In this range of r, expression (A1.1) should take also the form of a combination of linearly independent solutions $r^{-1/2}J_{2\lambda_l+1}[(8r)^{1/2}]$ and $r^{-1/2}N_{2\lambda_l+1}[(8r)^{1/2}]$. The coefficients in this combination are determined from the condition of matching to (A1.1), by using the asymptotes of cylindrical functions. The result, apart from normalization, takes the form (2.16).

APPENDIX 2

In second-order perturbation theory the equivalent operator for a quadrupole potential includes a monopole ($q=0$), a quadrupole ($q=2$), and an octupole ($q=4$):

$$\begin{aligned}
&\langle l\|W_0\|l\rangle \\
&=\frac{[5(2l+1)]^{1/2}}{4\pi}\left\{\frac{3(l+1)(l+2)}{2(2l+1)(2l+3)}(R_{nl}|r^{-3}g_{l+2}r^{-3}|R_{nl})\right. \\
&\quad+\frac{3l(l-1)}{2(2l-1)(2l+1)}(R_{nl}|r^{-3}g_{l-2}r^{-3}|R_{nl}) \\
&\quad\left.+\frac{l(l+1)}{(2l-1)(2l+3)}(R_{nl}|r^{-3}g_{l}r^{-3}|R_{nl})\right\}, \\
&\langle l\|W_2\|l\rangle \\
&=\frac{5}{4\pi}\left(\frac{l(l+1)(2l+1)}{14}\right)^{1/2}\left\{\frac{3(l+2)}{(2l+1)(2l+3)}\left(\frac{2l-1}{2l+3}\right)^{1/2}\right. \\
&\quad\times(R_{nl}|r^{-3}g_{l+2}r^{-3}|R_{nl})+\frac{3(l-1)}{(2l-1)(2l+1)}\left(\frac{2l+3}{2l-1}\right)^{1/2} \\
&\quad\times(R_{nl}|r^{-3}g_{l-2}r^{-3}|R_{nl}) \\
&\quad\left.+\frac{15-4l(l+1)}{(2l-1)^{1/2}(2l+3)^{1/2}}(R_{nl}|r^{-3}g_{l}r^{-3}|R_{nl})\right\}, \\
&\langle l\|W_4\|l\rangle \\
&=\frac{15(2l+1)}{8\pi}\left[\frac{(l-1)l(l+1)(l+2)}{70(2l-3)(2l-1)(2l+1)(2l+3)(2l+5)}\right]^{1/2} \\
&\quad\times\left\{\frac{(2l-1)(2l-3)}{(2l+1)(2l+3)}(R_{nl}|r^{-3}g_{l+2}r^{-3}|R_{nl})+\frac{(2l+3)(2l+5)}{(2l-1)(2l+1)}\right. \\
&\quad\times(R_{nl}|r^{-3}g_{l-2}r^{-3}|R_{nl}) \\
&\quad\left.+4\frac{(2l-3)(2l+5)}{(2l-1)(2l+3)}(R_{nl}|r^{-3}g_{l}r^{-3}|R_{nl})\right\}, \qquad \text{(A2.1)} \\
&\langle l+2\|W_4\|l\rangle=-\frac{15}{8\pi(2l+3)}\left(\frac{l(l+1)(l+2)(l+3)}{7(2l-1)(2l+3)(2l+7)}\right)^{1/2} \\
&\quad\times\{(2l+7)(R_{nl+2}|r^{-3}g_{l}r^{-3}|R_{nl}) \\
&\quad+(2l-1)(R_{nl+2}|r^{-3}g_{l+2}r^{-3}|R_{nl})\}, \\
&\langle l+4\|W_4\|l\rangle \\
&=\frac{15}{8\pi}\left(\frac{(l+1)(l+2)(l+3)(l+4)}{(2l+3)(2l+5)(2l+7)}\right)^{1/2}(R_{nl+4}|r^{-3}g_{l+2}r^{-3}|R_{nl}).
\end{aligned}$$

The general expression for the radial matrix elements turns out to be quite unwieldy. We present here only the results for a pure Coulomb unperturbed potential:

$$\begin{aligned}
&(R_{nl}|r^{-3}g_{l+2}r^{-3}|R_{nl}) \\
&=\frac{20}{3n^3l(l+1)(l+2)(2l-1)(2l+1)(2l+3)}, \\
&(R_{nl}|r^{-3}g_{l-2}r^{-3}|R_{nl}) \\
&=-\frac{20}{3n^3(l-1)l(l+1)(2l-1)(2l+1)(2l+3)}, \qquad \text{(A2.2)} \\
&(R_{nl}|r^{-3}g_{l}r^{-3}|R_{nl})=\frac{15(2l+1)^4-35(2l+1)^2+8}{2n^3(2l+1)^3l^3(l+1)^3(2l-1)(2l+3)} \\
&(R_{nl+2}|r^{-3}g_{l+2}r^{-3}|R_{nl}) \\
&=\frac{10}{3n^3(l+1)(l+2)(l+3)(2l+1)(2l+3)(2l+5)} \\
&(R_{nl+4}|r^{-3}g_{l+2}r^{-3}|R_{nl})=0.
\end{aligned}$$

In this case

$$\langle l+2\|W_2\|l\rangle=\langle l+4\|W_4\|l\rangle=0. \qquad \text{(A2.3)}$$

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