

higher excited states. In fact, for the first three P states the polarizabilities in the $(n+1)$ st excited state are roughly ten times those in the n th excited state. Both this effect and (b) arise from the fact that a less strongly bound valence electron is more easily distorted by the field.

(d) The scalar polarizability α_0 is roughly ten times the tensor polarizability α_2 . Thus the differential shift among magnetic substates is only about a tenth of the absolute shift of all the substates.

(e) All $\alpha_0 > 0$ and all $\alpha_2 < 0$, except for the higher ${}^2P_{3/2}$ states of Na, which are strongly perturbed by D states lying at slightly lower energies. Perturbing states tend to repel the perturbed state, so states above the ${}^2P_{3/2}$ energy tend to depress that level, states below tend to raise it. But since the

higher states usually predominate in their contributions to α_0 we generally find that the levels are pushed to lower energy, i. e., $\alpha_0 > 0$. In the case of Na, one D state lies just below the $P_{3/2}$ state, and yields a large negative contribution to α_0 .

(f) The S states contribute little to the polarizabilities. This is a fortuitous circumstance that occurs because the ${}^2P_{3/2}$ states lie roughly midway between the nearest S states, so their contributions to α_0 and α_2 very nearly cancel. This is readily seen in Table I.

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Perturbation of a Decaying State*

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One intuitively expects that a long-lived decaying state must have many properties like those of true eigenstates, with interesting technical modifications to encompass the complex energy. We examine here the small change in the complex energy due to the application of a weak perturbation.

Apparently, the energy levels of a quantum system fall into two distinct groups, the discrete and continuous spectra. An intermediate possibility exists, however, which unites some aspects of both. This possibility, which occurs in a wide variety of

atomic and nuclear systems, is the decaying state. Here the spectrum is, strictly speaking, continuous; nevertheless a carefully prepared superposition of continuum states behaves, for a time, very much like a discrete eigenstate. To each decaying

state we can usefully assign a complex energy

$$E_c = E_0 + i\Gamma.$$

We may precisely define this complex energy as the location of a pole of the appropriate Green's function; the pole is, technically speaking, on a second sheet, separated from the real axis by the imaginary part Γ . There is a simple interpretation for Γ ; its reciprocal indicates the lifetime of the decaying state.

We intuitively expect that a decaying state must have many properties like those of discrete eigenstates, with interesting modifications to encompass the complex energy. We examine here the small change in the complex energy E_c due to the application of a weak perturbation.

This is not the usual perturbation theory of discrete eigenstates; both the real part and the imaginary part of the complex energy E_c alter. We have obtained an exact formula for these alterations, in a special context. The result is

$$E_c = E_c^{(0)} + \lambda \int_0^\infty \phi_0^2(r) u(r) dr + O(\lambda^2). \quad (1)$$

Here $\lambda u(r)$ is the perturbation, and $E_c^{(0)}$ and $\phi_0(r)$ are the complex energy and "wave function" for the unperturbed decaying state. We define these below.

It is not surprising that the change in E_c is linear in λ , the strength of the perturbation. However the integral which appears in Eq. (1) is interesting because it is not the usual Hermitian (diagonal) matrix element. The wave function $\phi_0(r)$ is complex, and its complex square appears in (1), rather than the squared absolute value. While it is mathematically obvious that an Hermitian expression would preclude a first-order alteration in Γ , still the physical significance of the non-Hermitian form (1) is unclear and intriguing.

In the present work, we concentrate our attention on a simple case which we may analyze exactly. We consider an electron in the presence of a central potential. The unperturbed potential $v(r)$ is assumed to have a barrier region which may trap the electron near the origin; the electron may tunnel through the barrier and this is responsible for the "decay." We describe the electron by an s -wave Schrödinger equation:

$$\left(-\frac{d^2}{dr^2} + v(r) + \lambda u(r) - k^2\right) \psi(r) = 0. \quad (2)$$

When we base our approach on the apparatus of scattering theory, we are taking the continuum viewpoint as fundamental.

The perturbation $\lambda u(r)$ is a central potential, influencing the electron within the barrier region. We assume that both $v(r)$ and $u(r)$ are strictly zero beyond a finite radius a .

With these assumptions, the Jost functions for the Schrödinger equation (2) have especially simple

properties.¹ We denote the exact Jost solution of the perturbed equation (2) by $f(k; r)$; it is that solution of Eq. (2) which equals e^{-ikr} for $r > a$. The Jost function is the value at the origin of the Jost solution:

$$f(k) \equiv f(k; 0).$$

Each of these definitions may also be used for complex values of k . With our assumptions about the potentials, $f(k)$ is analytic for all k .¹

The decaying states of this system are associated with zeros of the Jost function in the upper-half k plane. We define the decay-state wave vector $K(\lambda)$ by the equation

$$f(K) = 0 \quad (3)$$

and the complex energy by $E_c = K^2$; we apply a subscript zero to denote the unperturbed values. The definition (3) is equivalent to the more usual Green's-function definition of a decaying state.

In this paper we only consider the first-order perturbation theory. We derive a result of the form (1) for a simple special perturbation:

$$\lambda u(r) = \lambda \delta(r - r_0) \quad r_0 < a. \quad (4)$$

This special case is easily dealt with; by the linearity of expression (1) it suggests the general result. Thus, the study of (4) provides a simple heuristic derivation of the perturbation formula. A mathematically sound (but more complicated) derivation of Eq. (1) is sketched in the Appendix.

For the perturbation (4), it is entirely elementary to relate the perturbed Jost solutions:

$$\begin{aligned} f(k; r) &= f_0(k; r) \quad \text{for } r > r_0 \\ &= A f_0(k; r) + B f_0(-k; r) \quad \text{for } r < r_0. \end{aligned}$$

We determine the numbers A, B by requiring continuity of $f(k; r)$ and the usual condition on the jump of its derivative. We simplify the formulas using the fact that the Wronskian of $f_0(k; r)$ and $f_0(-k; r)$ is constant. We find

$$\begin{aligned} A &= 1 + (\lambda/2ik) f_0(k; r_0) f_0(-k; r_0), \\ B &= -(\lambda/2ik) f_0^2(k; r_0). \end{aligned}$$

The dependence of $K(\lambda)$ upon λ is implicitly determined by Eq. (3). If we differentiate Eq. (3) with respect to λ , and evaluate the result for $\lambda = 0$, we obtain

$$\left(\frac{dK}{d\lambda}\right)_0 = \left[f_0(-K_0) / 2iK_0 \left(\frac{df_0}{dk}\right)_{K_0} \right] f_0^2(K_0; r_0).$$

(The derivative on the left-hand side is evaluated for $\lambda = 0$.) We rewrite this formula in the form

$$\frac{d}{d\lambda} (K^2) = -i \left[f_0(-K_0) / \left(\frac{\partial f_0}{\partial K_0}\right) \right] \int_0^\infty f_0^2(K_0; r) u(r) dr.$$

Now we define the wave function for the decaying state by the equation

$$\phi_0(r) \equiv \left\{ -i \left[f_0(-K_0) / \left(\frac{\partial f_0}{\partial K_0} \right) \right] \right\}^{1/2} f_0(K_0; r), \quad (5)$$

and then Eq. (1) follows.

The result (1) is an analog of the Feynman-Hellmann theorem. We expect that a similar result can be formulated for other problems, where the decay mechanism is more interesting.

A physical example of the latter type is the following. Consider an excited atom in a magnetic field. It is well known that there is a linear alteration in the real part E_r of the excited-state energy due to the magnetic field; this leads to the Zeeman effect. However the imaginary part Γ is also weakly field dependent. Even if the dipole radiation matrix element is not altered (to first order) by the magnetic field, the photon density of states certainly has a first-order alteration. This causes a change in the decay rate, i. e., the natural line-width. Of course, for optical spectra such an effect is far too small to be observable.

Our result (1) may also be obtained by a slightly more complicated method involving the Green's function for the Schrödinger equation (2). We may express this Green's function in terms of the Jost solutions and thereby analytically continue it onto the second sheet (i. e., to the upper-half k plane). The usual continuum perturbation theory for this Green's function thereby transforms into a decay-state perturbation theory, which has complex energies in the denominators and matrix elements of the form

$$U_{nm} = \lambda \int_0^\infty \phi_n(r) u(r) \phi_m(r) dr$$

in the numerators (n, m refer to the various decay states). However, there are serious technical difficulties in handling this expansion; these difficulties are due to the absence of orthogonality and normalization theorems for the decay-state wave functions.

The wave functions (8) cannot be normalized; this is an important difference between the decay-state problem and the usual discrete-state perturbation theory. However the matrix elements appearing [e. g., in Eq. (1) above] are finite. They are rendered convergent by the properties of the potential.

In conclusion, we see that while the result (1) looks superficially like the discrete-state perturbation formula, it is obtained only by an indirect route which carefully avoids such undefined concepts as normalization and orthogonality of the decay-state wave functions.

The idea of this inquiry was suggested by Professor E. Gerjuoy.

APPENDIX

In this appendix, we supply a general proof of (1) which altogether avoids the use of a δ -function perturbation. It is thus more mathematically rigorous than the discussion given in the text, although considerably more ungainly and complicated.

We compare the differential equations defining the perturbed and unperturbed Jost solutions:

$$\begin{aligned} -f''(k; \lambda; r) + [v(r) + \lambda u(r) - k^2] f(k; \lambda; r) &= 0, \\ -f_0''(K_0; r) + [v(r) - K_0^2] f_0(K_0; r) &= 0. \end{aligned}$$

The primes refer to differentiation with respect to r . As above, we define the unperturbed wave vector K_0 by the condition $f_0(K_0; 0) = 0$. We multiply the first equation by $f_0(K_0; r)$ and the second equation by $f(k; \lambda; r)$, subtract the second from the first, and integrate from $r = 0$ up to $r = a$. The result is

$$\begin{aligned} \int_0^a [K_0^2 - k^2 - \lambda u(r)] f_0(K_0; r) f(k; \lambda; r) dr \\ = [f(k; \lambda; r) f_0'(K_0; r) - f'(k; \lambda; r) f_0(K_0; r)] \Big|_0^a. \quad (6) \end{aligned}$$

Using Eq. (6), we perform two procedures. The first is to set k equal to $K(\lambda)$, for which $f(K; \lambda; 0)$ is zero. The right-hand side of Eq. (6) is then, using the known form of $f(K; \lambda; r)$ for $r \geq a$,

$$i(K - K_0) \exp(-iK_0 a - iKa). \quad (6')$$

We differentiate Eq. (6) with respect to λ , and set $\lambda = 0$. Here we are assuming that the derivatives involved exist, a question similar to the assumption that the perturbation series is convergent. While interesting, such questions are not essential to establishing the form of the series when it does exist. After we have set $\lambda = 0$, we obtain

$$\begin{aligned} -2K_0 \left(\frac{\partial K}{\partial \lambda} \right)_0 \int_0^a f_0^2(K_0; r) dr \\ + \int_0^a u(r) f_0^2(K_0; r) dr = i \left(\frac{\partial K}{\partial \lambda} \right)_0 e^{-2iK_0 a}. \quad (7) \end{aligned}$$

Now we return to Eq. (6). Our second procedure is to set $\lambda = 0$, leaving k arbitrary. We obtain

$$\begin{aligned} \int_0^a (K_0^2 - k^2) f_0(K_0; r) f_0(k; r) dr \\ = [f_0(k; r) f_0'(K_0; r) - f_0'(k; r) f_0(K_0; r)] \Big|_0^a. \quad (8) \end{aligned}$$

The right-hand side now is a quantity like (6'), with k replacing K , plus an additional contribution from $r = 0$, because $f_0(k; r)$ is not zero there. Setting $k = -K_0$, we obtain

$$-f'(K_0; 0) = 2iK_0 / f_0(-K_0). \quad (9)$$

Finally, we differentiate Eq. (8) with respect to k , and then set $k = K_0$. The result, simplified using

Eq. (9), is

$$-2K_0 \int_0^a f_0^2(K_0; r) dr = i \exp(-2iK_0 a) - \frac{2iK_0}{f_0(-K_0)} \left(\frac{\partial f_0}{\partial k} \right)_{k_0}, \quad (10)$$

and this in conjunction with Eq. (7) establishes the original perturbation formula (1).

We see that the heuristic calculation of the text, based upon the δ -function potential (4), has correctly obtained the form of the general result. The derivation given in this appendix only assumes that $v(r) + \lambda u(r)$ obey the usual analytic conditions required for Poincaré's theorem.¹

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Hyperfine Structure of the Ground State of Mn⁵⁵†

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The five hyperfine transition frequencies of the $S_{5/2}$ ground state of Mn⁵⁵ have been measured in a spin-exchange optical pumping experiment. The optical pumping flasks contained a neon buffer gas, and the measurements were made as a function of buffer-gas pressure. The measurements were carried out at a temperature of 700 °C. The linewidth of the Mn signal was typically 300 Hz. The hyperfine interaction constants were found to be $A = -72\,420\,836$ (15) Hz, $B = -19\,031$ (17) Hz, $C = -0.7 \pm 1.1$ Hz, $|D| < 0.25$ Hz, and $|E| < 0.02$ Hz. The fractional pressure shift in A was found to be $(1/A)(\partial A/\partial P) = (2.6 \pm 0.2) \times 10^{-8}$ Torr⁻¹. No pressure dependence of the other interaction constants was observed.

I. INTRODUCTION

The hyperfine structure of the $S_{5/2}$ ground state ($I = \frac{5}{2}$, $J = \frac{5}{2}$) of Mn⁵⁵ has previously been investigated by atomic-beam methods.^{1,2} There are five hyperfine transition frequencies from which one can determine five interaction constants in the Hamiltonian. First-order perturbation theory relates these constants to electric and magnetic multipole interactions for atoms where LS coupling is a good approximation. In many cases, however, relativistic effects, configuration mixing, and higher-order perturbation terms contribute significantly to the interaction constants. In this case, measurement of the interaction constants can lead to a refinement of theoretical wave functions.

In the most recent atomic-beam experiment,² three hyperfine frequencies were measured to determine the magnetic dipole and electric quadrupole interaction constants A and B . The three remaining constants were set equal to zero. The value of B was attributed entirely to relativistic corrections.

We report here a more precise spin-exchange optical pumping experiment in which all five hyperfine frequencies were measured, eliminating the need to set any of the interaction constants equal to zero.

The Mn atoms were polarized in a weak magnetic field by spin-exchange collisions with optically pumped Rb atoms. When an rf field induces hyperfine transitions in the Mn atoms, they are depolarized and the spin-exchange collisions depolarize the Rb atoms. This results in a change in the intensity of the pumping light transmitted by the sample flask. Due to the low vapor pressure of Mn, the measurements were performed at temperatures near 700 °C. The density of the Rb atoms in the flask was controlled independently of the flask temperature in a manner described in a previous publication.³

II. APPARATUS

A block diagram of the apparatus is shown in Fig. 1. The magnetic field was produced by Helmholtz coils situated inside two concentric cylindrical magnetic shields. The sample flasks were 300-ml quartz spheres. They were heated to 700 °C in a firebrick oven located in the center of the shields. The oven was heated with electrical heating rods. The Mn vapor pressure at this temperature is approximately 1×10^{-6} Torr. The Rb density in the flask was adjusted for optimum signal strength in the following way. A reservoir of Rb metal was contained in a small sidearm attached to the flask