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Perturbation theory of resonant states induced by an electrostatic field: one-dimensional model

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Abstract. The behaviour of an electron in an attractive potential placed in a uniform external electrostatic field is studied in a one-dimensional model. The time development of the state is obtained through the evolution operator, which can be expressed in terms of resonant outgoing-wave energy eigenfunctions with complex energies. The theory, perturbative and non-perturbative, is developed with the aid of Kapur–Peierls eigenfunctions and Bloch's boundary-condition operator. If ψ_{RS} and E_{RS} denote the usual standard Rayleigh–Schrödinger expansions for the Stark effect, which are asymptotic power series in the field strength F for the real parts of the wavefunction and energy, then one result is that the negative of the imaginary part of the complex energy of the resonant state has the (asymptotic) perturbation theory formula

$$\Gamma \sim \frac{\phi_{RS}(a)^2}{\int_0^\infty \phi_{RS}(x)^2\,dx} F^{1/3}(\hbar^2/2m)^{2/3}\pi^{-1}\,\mathrm{Bi}[-(2mF/\hbar^2)^{1/3}(a + E_{RS}/F)]^{-2}$$

$$\sim (\hbar^2\kappa/2m)\phi_{RS}(a)^2 \exp(2\kappa a - 2\kappa^3\hbar^2/3mF)\left(\int_0^a \phi_{RS}(x)^2\,dx\right)^{-1}$$

which may be interpreted as the probability of reaching a point inside the classically forbidden region, times a decay factor that is independent of the system.

Here Bi denotes the (second) Airy function, a is any value of x outside the range of the attractive potential, and κ is $(-2mE_{RS}/\hbar^2)^{1/2}$. The case of an attractive square-well potential is treated as a numerical example.

1. Introduction

In a uniform external electrostatic field, the energy levels of an atom or molecule shift, split and broaden. The broadening is a consequence of 'field ionisation': an electron initially localised near a nucleus can tunnel through the potential barrier into the distant classically allowed region. Thus, when the field is turned on, the zero-field bound states turn into metastable states.

The theory of the field ionisation of the hydrogen atom was first treated by Oppenheimer (1928), who obtained a 'golden-rule' type formula for the ionisation rate. Lanczos (1930a,b, 1931) and later Rice and Good (1962), treated the problem by the JWKB method. More recent treatments based on numerical methods (Fauchier and Dow 1974, Hehenberger *et al* 1974, Froelich and Brändas 1975, Gushina and

Nikulin 1975) have considered more accurately the field dependence of the energies, of the widths, and of the intensities of the spectral lines. A different approach was taken by Duke and Alferieff (1966), who neglected the uniform field near the nucleus and the Coulomb field far away.

Another point of departure is to study the disappearance of the continuous spectrum and appearance of the discrete spectrum as the field strength F goes from a non-zero to a zero value as 'isolated spectral concentration' (Friedrichs 1965).

In order to clarify the effect of a uniform field on a system initially possessing bound states, we develop a theory for resonant states in a one-dimensional model. We assume a potential with a finite range, so that in the exterior region the wavefunction in the presence of the uniform field has a known form. The role of the purely 'outgoing-wave eigenfunctions' and their complex energies is introduced via the time-dependent behaviour of the system and the evolution operator. To further clarify the nature of the 'outgoing-wave eigenfunctions' and to develop a formalism more suitable for computations, we turn to the theory of nuclear reactions of Kapur and Peierls (1938), which treats the representation of the wavefunction in the interior region by a discrete method.

We discuss the solution of the complex eigenvalue problem by perturbation theory, indicating in particular the changes required to obtain a complex result. Although we are primarily concerned with the imaginary part of the complex energy, we see in a rather transparent way that the real part of the perturbation series—the usual Rayleigh–Schrödinger series—is an asymptotic expansion for the real part of the complex energy. The complex perturbation theory differs from the usual Rayleigh–Schrödinger theory in that there are two series—dominant and subdominant—and in part, the perturbation appears in the boundary condition. To handle the perturbation of the boundary condition, the 'boundary-condition operator' of Bloch (1957) is indispensable.

Illustrative numerical results are given for a square-well potential.

2. Field ionisation: formal theory

2.1. The role of outgoing-wave energy eigenfunctions

Consider an electron initially bound in a (real) one-dimensional potential well $V_0(x)$ of finite range a, placed in a uniform electrostatic field $-F/e$, as illustrated in figure 1. For large enough x, the potential $V(x) = V_0(x) - Fx$ is always less than the energy E, so that the electron will tunnel through the 'barrier' and ionise.

To describe the ionisation process, one must solve the Schrödinger equation for the time-dependent wavefunction $\Psi(x, t)$, and then show that under suitable conditions the probability density in the interior region decays exponentially with time

$$|\Psi(x, t)|^2 \sim f(x) \exp(-2t\Gamma/\hbar) \qquad (0 \leqslant x \leqslant a). \tag{1}$$

Such a formula can be obtained, following Frey and Thiele (1968), from the expansion of $\Psi(x, t)$ on the energy eigenfunctions $\chi(x, E)$, suitably normalised, through the evolution operator $U(x, x', t)$

$$\Psi(x, t) = \int_0^\infty \mathrm{d}x'\, U(x, x', t)\Psi(x', 0) \tag{2}$$

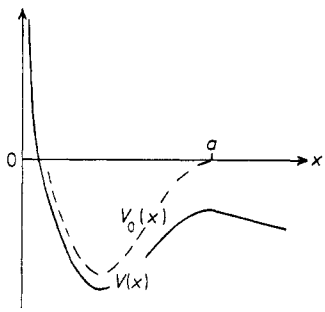

Figure 1. The general shape of the potential.

$$U(x, x', t) = \int_{-\infty}^{\infty} \mathrm{d}E\, \chi(x, E)\, [\chi(x', E^*)]^* \exp(-\mathrm{i}Et/\hbar). \tag{3}$$

Here the asterisk denotes complex conjugation. The apparently superfluous asterisk on the E is to ensure that if χ is an analytic function of E, then so is the integrand. In the exterior region ($x \geqslant a$), $\chi(x, E)$ is a linear combination of Airy functions. With 'outgoing' and 'incoming' Airy functions $\mathscr{Ai}^{(\pm)}$, whose properties will be developed later, we may write $\chi(x, E)$ in the following form, which satisfies the usual delta-function normalisation:

$$\chi(x, E) = [m^{1/3}(2\hbar)^{-2/3}F^{-1/6}]\, [C_+(E)\mathscr{Ai}^{(+)}(-\xi) + C_-(E)\mathscr{Ai}^{(-)}(-\xi)]/C_-(E) \tag{4}$$

$$= [m^{1/3}(2\hbar)^{-2/3}F^{-1/6}]\, \psi(x, E)/C_-(E) \tag{5}$$

where $\psi(x, E)$ is real for real E, and

$$C_+(E) = [C_-(E^*)]^*. \tag{6}$$

If the integration path in the resulting formula for U,

$$U(x, x', t) = (m/4\hbar^2)^{2/3}F^{-1/3} \int_{-\infty}^{\infty} \mathrm{d}E\, \psi(x, E)\, \psi(x', E) \exp(-\mathrm{i}Et/\hbar)/[C_+(E)C_-(E)] \tag{7}$$

can be 'closed at ∞' in the lower half of the E plane, as the exponential factor would suggest, and if the only singularities of the integrand in the lower half plane are from simple zeros W_n of $C_-(E)$ (see below), then one has from the residue theorem

$$U(x, x', t) = -2\pi\mathrm{i}(m/4\hbar^2)^{2/3}F^{-1/3} \sum_n \frac{\psi(x, W_n)\, \psi(x', W_n) \exp(-\mathrm{i}W_n t/\hbar)}{C_+(W_n)(\mathrm{d}/\mathrm{d}W_n)C_-(W_n)}. \tag{8}$$

One then obtains equation (1) if only one term is dominant, with $-\Gamma$ being the imaginary part of the dominant W_n.

The complex energy W_n is an energy eigenvalue corresponding to a 'purely outgoing-wave' boundary condition in the exterior region, since $C_-(W_n) = 0$. Thus the 'outgoing-wave eigenfunctions' play the same role as in the case of field-free tunnelling through a barrier (Siegert 1939).

We shall not try to make the above argument too much more rigorous, but the ingredients of such an effort would include establishing: $\psi(x, E)$ is an entire function of E; $C_+(E)$ cannot have zeros in the lower half plane, otherwise $\psi(x, E)$

would be a square-integrable wavefunction with a non-real energy; for large E, $(E \gg Fx)$, $\psi(x, E) \sim \sin(\sqrt{2mE/\hbar^2}x + \delta)$.

To aid in calculating $\psi(x, E)$ and the W_n, we turn to the approach of Kapur and Peierls (1938) and Bloch (1957).

2.2. *Kapur–Peierls eigenfunctions; Bloch's boundary-condition operator*

To solve the Schrödinger equation,

$$0 = (H - E)\psi(x, E) \tag{9}$$

$$= [-(\hbar^2/2m)(\mathrm{d}/\mathrm{d}x)^2 + V_0(x) - Fx - E]\psi(x, E) \qquad (0 \leqslant x \leqslant a) \tag{10}$$

$$= [-(\hbar^2/2m)(\mathrm{d}/\mathrm{d}x)^2 - Fx - E]\psi(x, E) \qquad (a \leqslant x < \infty) \tag{11}$$

with the boundary conditions

$$\psi(0, E) = 0 \tag{12}$$

$$\psi'(x, E)/\psi(x, E) \text{ continuous at } x = a \tag{13}$$

it is necessary to find a representation for the wavefunction in the interior region, and then to determine the ratio of the coefficients of the Airy functions by matching logarithmic derivatives at $x = a$. In the field-free case, Kapur and Peierls (1938) let H itself generate a basis set of discrete eigenfunctions for the interior region by imposing an outgoing-wave boundary condition at $x = a$, namely, that the logarithmic derivative be ik, where k is the wavevector. To carry out a parallel treatment here requires first a specification of the 'outgoing' and 'incoming' Airy functions.

We define the 'outgoing' and 'incoming' Airy functions in terms of the standard Airy functions Ai and Bi (Antosiewicz 1965) by

$$\mathscr{A}i^{(\pm)}(z) = \mathrm{Bi}(z) \pm \mathrm{i}\mathrm{Ai}(z). \tag{14}$$

As $z \to -\infty$, $\mathscr{A}i^{(\pm)}(z)$ have the asymptotic expansions

$$\mathscr{A}i^{(\pm)}(z) \sim \pi^{-1/2}(-z)^{-1/4} \exp\{\pm \mathrm{i}[\tfrac{2}{3}(-z)^{3/2} + \tfrac{1}{4}\pi]\}\left(1 + \sum_{k=1}^{\infty} c_k[\pm \mathrm{i}\tfrac{2}{3}(-z)^{3/2}]^{-k}\right)$$

$$(z \to -\infty). \tag{15}$$

(The c_k are given by Antosiewicz 1965 p 448.) With ξ defined by

$$\xi = (2mF/\hbar^2)^{1/3}(x + E/F) \tag{16}$$

the $\mathscr{A}i^{(\pm)}(-\xi)$ are solutions of equation (11). We denote the logarithmic derivative of $\mathscr{A}i^{(+)}(-\xi)$ at $x = a$ by $g^{(+)}(E)$:

$$g^{(+)}(E) \equiv [(\mathrm{d}/\mathrm{d}x) \ln \mathscr{A}i^{(+)}(-\xi)]_{x=a}. \tag{17}$$

The analogous Kapur–Peierls (KP) eigenfunctions and boundary condition are fixed by

$$H\phi_n(x, E) = \omega_n(E)\phi_n(x, E) \qquad (0 \leqslant x \leqslant a) \tag{18}$$

$$[(\mathrm{d}/\mathrm{d}x) \ln \phi_n(x, E)]_{x=a} = g^{(+)}(E). \tag{19}$$

The KP eigenfunctions are well suited for representing $\psi(x, E)$ in the interior region, and the expansion coefficients are proportional to $C_-(E)$, the coefficient of $\mathscr{A}i^{(-)}(-\xi)$ in the exterior region

$$\psi(x, E) = \sum_n c_n(E)\phi_n(x, E) \qquad (0 \leqslant x \leqslant a) \tag{20}$$

$$c_n(E) = C_-(E)(\hbar^2/m)^{2/3}(2F)^{1/3}(\mathrm{i}/\pi)\phi_n(a, E)\{\mathscr{A}i^{(+)}(-\xi_a)N_n(E)[E - \omega_n(E)]\}^{-1} \tag{21}$$

where

$$N_n(E) = \int_0^a \phi_n(x, E)^2 \, \mathrm{d}x \tag{22}$$

$$\xi_a = (2mF/\hbar^2)^{1/3}(a + E/F). \tag{23}$$

To establish the expansion (20) and (21), it is necessary to discuss some of the properties of the KP eigenfunctions.

Because the boundary condition depends on E through $g^{(+)}(E)$, both the KP eigenvalues and eigenfunctions depend on E. In effect, the basis set changes with E.

Because $g^{(+)}(E)$ is complex, H is not Hermitian on $[0, a]$. Thus the $\omega_n(E)$ are not real, and the KP eigenfunctions $\phi_n(x, E)$ are not orthogonal with the usual (complex) scalar product. They do, however, satisfy a 'real' orthogonality relation:

$$\int_0^a \phi_n(x, E)\phi_m(x, E) \, \mathrm{d}x = N_n(E)\delta_{nm}. \tag{24}$$

We assume that the $\{\phi_n\}$ form a complete set:

$$\sum_n \frac{\phi_n(x, E)\phi_n(x', E)}{N_n(E)} = \delta(x - x'). \tag{25}$$

In his elegant reformulation of the KP method, Bloch (1957) introduced a so-called *boundary-condition operator* $\mathscr{L}$ that, when added to H, gave a 'real self-adjoint' sum. (For an English version of Bloch's work, see McCarthy (1968).) Here we define $\mathscr{L}$ by

$$\mathscr{L} \equiv (\hbar^2/2m)\delta(x - a)[(\mathrm{d}/\mathrm{d}x) - g^{(+)}(E)] \tag{26}$$

with the convention that

$$\int_0^a f(x)\delta(x - a) \, \mathrm{d}x = f(a). \tag{27}$$

(We shall not integrate $\mathscr{L}$ further than a.) If $\eta(x)$ and $\zeta(x)$ are two arbitrary functions that vanish at $x = 0$, then $H + \mathscr{L}$ is 'real self-adjoint' in the sense that

$$\int_0^a \eta(x)(H + \mathscr{L})\zeta(x) \, \mathrm{d}x$$

$$= \int_0^a \zeta(x)(H + \mathscr{L})\eta(x) \, \mathrm{d}x \tag{28}$$

$$= \int_0^a [(\hbar^2/2m)(\mathrm{d}\eta/\mathrm{d}x)(\mathrm{d}\zeta/\mathrm{d}x) + (V_0(x) - Fx)\eta\zeta] \, \mathrm{d}x$$

$$- (\hbar^2/2m)g^{(+)}(E)\eta(a)\zeta(a). \tag{29}$$

The two equations (18) and (19) can be replaced by the single equation

$$(H + \mathscr{L})\phi_n(x, E) = \omega_n(E)\phi_n(x, E) \qquad (0 \leqslant x \leqslant a) \tag{30}$$

since the above equation holds at $x = a$ only if $\phi_n(x, E)$ satisfies equation (19).

Consider now the Schrödinger equation in the form

$$(E - H - \mathscr{L})\psi(x, E) = -\mathscr{L}\psi(x, E) \tag{31}$$

$$\psi(x, E) = -(E - H - \mathscr{L})^{-1}\mathscr{L}\psi(x, E) \tag{32}$$

$$c_n(E) = \int_0^a \mathrm{d}x\, \phi_n(x, E)\psi(x, E)/N_n(E) \tag{33}$$

$$= -[E - \omega_n(E)]^{-1} \int_0^a \mathrm{d}x\, \phi_n(x, E)\mathscr{L}\psi(x, E)/N_n(E). \tag{34}$$

The final integral is easily evaluated. Note that

$$\mathscr{L}\mathscr{A}i^{(+)}(-\xi) = 0 \tag{35}$$

$$\mathscr{L}\mathscr{A}i^{(-)}(-\xi) = (\hbar^2/m)^{2/3}(2F)^{1/3}(-\mathrm{i}/\pi)\delta(x - a)/\mathscr{A}i^{(+)}(-\xi_a) \tag{36}$$

$$\mathscr{L}\psi(x, E) = C_-(E)\mathscr{L}\mathscr{A}i^{(-)}(-\xi) \tag{37}$$

so that

$$-\int_0^a \mathrm{d}x\, \phi_n(x, E)\mathscr{L}\psi(x, E) = C_-(E)(\hbar^2/m)^{2/3}(2F)^{1/3}(\mathrm{i}/\pi)\phi_n(a, E)/\mathscr{A}i^{(+)}(-\xi_a) \tag{38}$$

which establishes the expansion formulae (20) and (21). Note that for equation (36), one needs the Wronskian relation,

$$\mathscr{A}i^{(+)}(-\xi)\,(\mathrm{d}/\mathrm{d}x)\mathscr{A}i^{(-)}(-\xi) - \mathscr{A}i^{(-)}(-\xi)\,(\mathrm{d}/\mathrm{d}x)\mathscr{A}i^{(+)}(-\xi) = (2mF/\hbar^2)^{1/3}(2/\pi\mathrm{i}). \tag{39}$$

We do not belabour questions of convergence, but we do wish to point out that in general the KP series (20) cannot converge uniformly at $x = a$. If E is not an outgoing-wave eigenvalue, then $C_-(E)$ is non-zero and the logarithmic derivative of $\psi(x, E)$ at $x = a$ is not $g^{(+)}(E)$:

$$(\mathrm{d}/\mathrm{d}a)\psi(a, E) \neq g^{(+)}(E)\psi(a, E) \qquad (E \neq W_n). \tag{40}$$

Yet every term in equation (20) does have a logarithmic derivative equal to $g^{(+)}(E)$ at $x = a$, so that the series cannot be differentiated term by term at $x = a$.

2.3. The S-matrix element and the W_n

The 'outgoing-wave eigenvalues' W_n are the zeros of $C_-(E)$. They are also the poles of the S-matrix element

$$S(E) \equiv C_+(E)/C_-(E) \tag{41}$$

$$= [\psi(a, E) - C_-(E)\mathscr{A}i^{(-)}(-\xi_a)]/[C_-(E)\mathscr{A}i^{(+)}(-\xi_a)] \tag{42}$$

$$= -\frac{\mathscr{A}i^{(-)}(-\xi_a)}{\mathscr{A}i^{(+)}(-\xi_a)} + \left(\frac{\hbar^2}{m}\right)^{2/3}(2F)^{1/3} \times \frac{\mathrm{i}}{\pi}\sum_n \frac{\phi_n(a, E)^2}{N_n(E)\mathscr{A}i^{(+)}(-\xi_a)^2[E - \omega_n(E)]}. \tag{43}$$

These poles occur where $E - \omega_n(E)$ vanishes:

$$W_n - \omega_n(W_n) = 0. \tag{44}$$

(There may be cases where $E - \omega_n(E)$ has more than one root, cf More and Gerjuoy (1973).) The assumption that $C_-(E)$ has only simple zeros is the assumption that the $E - \omega_n(E)$ have only simple zeros.

2.4. *Formulae for* $(d/dW_n)C_-(W_n)$ *and* $U(x, x', t)$

The KP expression (43) for $C_+(E)/C_-(E)$ leads to a formula for the $(\mathrm{d}/\mathrm{d}W_n)C_-(W_n)$ that occurs in equation (8) for U:

$$\mathrm{d}C_-(W_n)/\mathrm{d}W_n = C_+(W_n)[1 - \omega_n'(W_n)]\,(-\mathrm{i}\pi)\left(\frac{\hbar^2}{m}\right)^{-2/3}(2F)^{-1/3}$$
$$\times N_n(W_n)\mathscr{A}i^{(+)}(-\xi_a)^2\phi_n(a, W_n)^{-2}. \tag{45}$$

Equations (43) and (21) also provide the formula for the expansion coefficient $c_m(W_n)$ (which formula can also be obtained by a very elementary argument)

$$c_m(W_n) = \delta_{nm}C_+(W_n)\mathscr{A}i^{(+)}(-\xi_a)/\phi_n(a, W_n). \tag{46}$$

Then we can rewrite equation (8) for U:

$$U(x, x', t) = \sum_n \frac{\phi_n(x, W_n)\phi_n(x', W_n)\exp(-\mathrm{i}W_n t/\hbar)}{N_n(W_n)[1 - \omega_n'(W_n)]}. \tag{47}$$

It should be noted that in general the $\phi_n(x, W_n)$ are not 'real orthogonal', because they are evaluated at different W_n:

$$\int_0^a \phi_n(x, W_n)\phi_m(x, W_m)\,\mathrm{d}x \neq 0 \qquad (m \neq n). \tag{48}$$

Thus there is no inconsistency from the presence of $\omega_n'(W_n)$ in equation (47). We obtain an even simpler formula (equations (51)–(53)) for $\omega_n'(W_n)$ in the next subsection.

2.5. *Variational principle for* $\omega_n(E)$; $\omega_n'(E)$

Since $H + \mathscr{L}$ is 'real self-adjoint' (equation (28)), $\omega_n(E)$ and $\phi_n(x, E)$ satisfy a stationary principle that could be exploited for calculations:

$$\delta\omega_n(E) = \delta\left(\int_0^a \phi_n(x, E)(H + \mathscr{L})\phi_n(x, E)\,\mathrm{d}x/N_n(E)\right) \tag{49}$$
$$= 0. \tag{50}$$

As a corollary, a (real) Hellmann–Feynman theorem is satisfied that yields a formula for $\omega_n'(E)$:

$$\omega_n'(E) = \int_0^a \phi_n(x, E)(\partial\mathscr{L}/\partial E)\phi_n(x, E)\,\mathrm{d}x/N_n(E) \tag{51}$$
$$= -(\hbar^2/2m)[\partial g^{(+)}(E)/\partial E]\phi_n(a, E)^2/N_n(E). \tag{52}$$

Moreover, $\partial g^{(+)}(E)/\partial E$ is a known function (equations (16), (17) and (11)):

$$\partial g^{(+)}(E)/\partial E = -(2m/\hbar^2)(a + E/F) - g^{(+)}(E)^2/F. \tag{53}$$

2.6. Estimates of Im $\omega_n(E)$ and Im W_n

We conclude this section with estimates of Im $\omega_n(E)$ and Im W_n. The aim is merely to show the signs and order of magnitude.

First take E to be real. Then, since the complex conjugate of equation (30) involves $\omega_n(E)^*$,

$$[H + \mathscr{L}^* - \omega_n(E)^*]\phi_n(x, E)^* = 0 \tag{54}$$

we obtain (using also equation (39) to evaluate the Wronskian)

$$\omega_n(E) - \omega_n(E)^* = \frac{\int_0^a \phi_n(x, E)^*[H + \mathscr{L} - H - \mathscr{L}^*]\phi_n(x, E)\mathrm{d}x}{\int_0^a |\phi_n(x, E)|^2\,\mathrm{d}x} \tag{55}$$

$$= \frac{-(\hbar^2/2m)|\phi_n(a, E)|^2[g^{(+)}(E) - g^{(+)}(E)^*]}{\int_0^a |\phi_n(x, E)|^2\,\mathrm{d}x} \tag{56}$$

$$= -\mathrm{i}(\hbar^2/2m)^{2/3}F^{1/3}(2/\pi)|\phi_n(a, E)|^2 \left(|\mathscr{A}i^{(+)}(-\xi_a)|^2 \int_0^a |\phi_n(x, E)|^2\,\mathrm{d}x\right)^{-1}$$

(E real). (57)

The imaginary part of ω_n is always negative for real E. The most interesting case is when E is negative and close to a bound-state energy level for vanishing F. For negative E and small enough F, $|\mathscr{A}i^{(+)}(-\xi_a)|^2 \sim \mathrm{Bi}(-\xi_a)^2$ and

$$\omega_n(E) - \omega_n(E)^* \sim -\mathrm{i}\frac{\hbar^2}{m}\kappa|\phi_n(a, E)|^2\left(\int_0^a |\phi_n(x, E)|^2\,\mathrm{d}x\right)^{-1} \exp[-\tfrac{2}{3}\kappa^3(mF/\hbar^2)^{-1} + 2a\kappa]$$

$$\times\left(1 - \frac{mF}{\hbar^2\kappa^3}(\tfrac{5}{12} + a\kappa + a^2\kappa^2) + \mathrm{O}(F^2)\right) \tag{58}$$

where

$$\kappa = (-2mE/\hbar^2)^{1/2}. \tag{59}$$

The strong exponential dependence, $\exp(-2\kappa^3\hbar^2/3mF)$, appears in virtually all calculations of field ionisation, and vanishes more rapidly than any power of F, as F approaches zero. The factor $\exp(2a\kappa)$ tends to make the result less dependent on a, for if x is greater than the range of the potential $V_0(x)$, then $\phi(x, E_0)\exp(\kappa x)$ is independent of x for $F = 0$, $x > a$, and E_0 a bound-state eigenvalue of H.

To estimate Im $W_n = -\Gamma_n$, we expect that Γ_n is $\mathrm{O}[\exp(-2\kappa^3\hbar^2/3mF)]$, and we write

$$W_n = E_n - \mathrm{i}\Gamma_n = \omega_n(W_n) \tag{60}$$

$$= \omega_n(E_n) - \mathrm{i}\Gamma_n\omega_n'(E_n) + \mathrm{O}(\Gamma_n^2) \tag{61}$$

$$\Gamma_n = -\mathrm{Im}\,\omega_n(E_n)/[1 - \mathrm{Re}\,\omega_n'(E_n)] + \mathrm{O}(\Gamma_n^2). \tag{62}$$

Note that equations (51)–(53), (60) and (61) imply that

$$E_n = \operatorname{Re} \omega_n(E_n) + O(\Gamma_n^2). \tag{63}$$

One may evaluate Γ_n explicitly by using equations (58) and (51)–(53), but we postpone doing so until later.

3. Perturbation theory

In the preceding section we have given an exact formulation for the resonant states of a one-dimensional electron in a uniform electrostatic field. In this section we take up the calculation of the key quantities of the formulation—the Kapur–Peierls eigenvalues $\omega_n(E)$ and the 'outgoing-wave eigenvalues' W_n—by perturbation theory. It is of particular interest how the usual Rayleigh–Schrödinger treatment of the Stark effect is related to the W_n, and how to calculate $-\Gamma_n$, the imaginary part of W_n—the field ionisation rate. The end result is a simple formula for Γ_n.

The Kapur–Peierls–Bloch approach of the preceding section reduces the eigenvalue problem (equations (9)–(11)) from the semi-infinite interval $[0, \infty)$, to the finite interval $[0, a]$, equation (30). The unperturbed problem corresponds to the Hamiltonian

$$\mathscr{H}^{(0)} = -(\hbar^2/2m)(\mathrm{d}/\mathrm{d}x)^2 + V_0(x) + \mathscr{L}^{(0)} \qquad (0 \leqslant x \leqslant a) \tag{64}$$

while the perturbation is the difference of $\mathscr{H}^{(0)}$ from

$$\begin{aligned} \mathscr{H} &\equiv H + \mathscr{L} \\ &= H^{(0)} - Fx + \mathscr{L} \end{aligned}$$

that is

$$\mathscr{H} - \mathscr{H}^{(0)} = -Fx + \mathscr{L} - \mathscr{L}^{(0)}. \tag{65}$$

A non-trivial difference between the ordinary perturbation problem and the present one is the perturbation in the boundary condition. Bloch's boundary-condition operator in effect recasts the boundary condition into the Hamiltonian so that it plays the role of a perturbation to the Hamiltonian.

We mention in passing the recent work of More (1971a,b) and More and Gerjuoy (1973), who developed a perturbation theory of resonant states in the field-free case. Their treatment is based on the Green's function, whereas ours is cast more in the mould of standard bound-state perturbation theory.

To treat $\mathscr{H} - \mathscr{H}^{(0)}$ as a perturbation, we must first develop an expansion for $\mathscr{L}$, the essence of which is an expansion for $g^{(+)}(E)$. It is convenient to break $g^{(+)}(E)$ into two parts:

$$g^{(+)}(E) = g_r(E) + \mathrm{i}g_i(E) \tag{66}$$

$$\begin{aligned} g_r(E) \equiv{}& (\mathrm{d}/\mathrm{d}a)\mathrm{Bi}(-\xi_a)/\mathrm{Bi}(-\xi_a) \\ &+ \pi^{-1}(2mF/\hbar^2)^{1/3}\,\mathrm{Ai}(-\xi_a)\,\mathrm{Bi}(-\xi_a)^{-1}\,[\mathrm{Bi}(-\xi_a)^2 + \mathrm{Ai}(-\xi_a)^2]^{-1} \end{aligned} \tag{67}$$

$$g_i(E) \equiv \pi^{-1}(2mF/\hbar^2)^{1/3}[\mathrm{Bi}(-\xi_a)^2 + \mathrm{Ai}(-\xi_a)^2]^{-1}. \tag{68}$$

Both $g_r(E)$ and $g_i(E)$ are real for real E (but not for complex E), and $g_i(E)$ is smaller than $g_r(E)$ by a factor $\exp(-2\kappa^3\hbar^2/3mF)$ for small F. From the standard

asymptotic expansions for Ai and Bi, we find that $g_r(E)$ has an asymptotic power series for small F, while $g_i(E)$ has an asymptotic power series times an exponential factor:

$$g_r(E) \sim (d/da)\,\mathrm{Bi}(-\xi_a)/\mathrm{Bi}(-\xi_a) \tag{69}$$

$$\sim -\kappa[1 - Fm\hbar^{-2}\kappa^{-3}(\tfrac{1}{2} + \kappa a) + O(F^2)] \quad [|\arg(-E)| < \pi/3, F \sim 0] \tag{70}$$

$$\sim \sum_n g_r^{(n)}(E)F^n \tag{71}$$

$$g_i(E) \sim \pi^{-1}(2mF/\hbar^2)^{1/3}\,\mathrm{Bi}(-\xi_a)^{-2} \tag{72}$$

$$\sim \kappa \exp(-2\kappa^3\hbar^2/3mF)\exp(2\kappa a)[1 - Fm\hbar^{-2}\kappa^{-3}(\tfrac{5}{12} + \kappa a + \kappa^2 a^2) + O(F^2)] \quad [|\arg(-E)| < \pi/3, F \sim 0] \tag{73}$$

$$\sim \exp(-2\kappa^3\hbar^2/3mF)\sum_n g_i^{(n)}(E)F^n. \tag{74}$$

If we make the usual Rayleigh–Schrödinger hypothesis that the wavefunction, the energy eigenvalue and the perturbation can be expressed as power series in F, then we lose the entire $g_i(E)$, which is the term in $\mathscr{H}$ that gives rise to the imaginary part of W_n. To retain $g_i(E)$, we must assume a more general form for the wavefunction and the energy eigenvalue, namely a power series plus $\exp(-2\beta/3F)$ times a power series, where

$$\beta = \kappa^3\hbar^2/m. \tag{75}$$

Consider specifically the Kapur–Peierls eigenfunction $\phi_n(x, E)$. We write

$$\phi_n(x, E) = \phi_{n,r}(x, E) + i\phi_{n,i}(x, E) \tag{76}$$

$$\phi_{n,r}(x, E) \sim \sum_l \phi_{n,r}^{(l)}(x, E)F^l \tag{77}$$

$$\phi_{n,i}(x, E) \sim \exp(-2\beta/3F)\sum_l \phi_{n,i}^{(l)}(x, E)F^l. \tag{78}$$

Similarly, we expand the KP eigenvalue

$$\omega_n(E) = \epsilon_n(E) + i\gamma_n(E) \tag{79}$$

$$\epsilon_n(E) \sim \sum_l \epsilon_n^{(l)}(E)F^l \tag{80}$$

$$\gamma_n(E) \sim \exp(-2\beta/3F)\sum_l \gamma_n^{(l)}(E)F^l \tag{81}$$

and the boundary-condition operator

$$\mathscr{L}(E) = \mathscr{L}_r + i\mathscr{L}_i \tag{82}$$

$$\mathscr{L}_r \sim \sum_l \mathscr{L}_r^{(l)}F^l \tag{83}$$

$$\mathscr{L}_{\mathrm{i}} \sim \exp(-2\beta/3F) \sum_{l} \mathscr{L}_{\mathrm{i}}^{(l)} F^{l} \tag{84}$$

$$\mathscr{L}_{\mathrm{r}}^{(l)} = (\hbar^2/2m)\delta(x-a)[\delta_{l0}(\mathrm{d}/\mathrm{d}x) - g_{\mathrm{r}}^{(l)}(E)] \tag{85}$$

$$\mathscr{L}_{\mathrm{i}}^{(l)} = -(\hbar^2/2m)\delta(x-a) g_{\mathrm{i}}^{(l)}(E). \tag{86}$$

Substitution of equations (76), (79) and (82) into the eigenvalue equation (30) and collection of terms of the same order in $\exp(-2\beta/3F)$ yield:

$$[H^{(0)} - Fx + \mathscr{L}_{\mathrm{r}} - \epsilon_n(E)]\phi_{n,\mathrm{r}}(x, E) = 0 \tag{87}$$

$$[H^{(0)} - Fx + \mathscr{L}_{\mathrm{r}} - \epsilon_n(E)]\phi_{n,\mathrm{i}}(x, E) + [\mathscr{L}_{\mathrm{i}} - \gamma_n(E)]\phi_{n,\mathrm{r}}(x, E) = 0. \tag{88}$$

The first equation (87), at least when E is real, has the form of an ordinary perturbation problem and can be solved by ordinary perturbation theory. We omit the details, because we shall shortly obtain a related but more important result. If we multiply the second equation (88) on the left by $\phi_{n,\mathrm{r}}(x, E)$ and integrate, we obtain

$$\gamma_n(E) \sim \frac{-g_{\mathrm{i}}(E)(\hbar^2/2m)\phi_{n,\mathrm{r}}(a, E)^2}{\int_0^a \phi_{n,\mathrm{r}}(x, E)^2 \,\mathrm{d}x} \tag{89}$$

which has the *implicit* form of $\exp(-2\beta/3F)$ times a power series in F, which form can be made explicit by expanding out $g_{\mathrm{i}}(E)$ and $\phi_{n,\mathrm{r}}(a, E)$. Equation (89) for $\gamma_n(E)$ is accurate to the first order in $\exp(-2\beta/3F)$. The same formula results from substituting $\phi_{n,\mathrm{r}}(x, E) + \mathrm{O}[\exp(-2\beta/3F)]$ for $\phi_n(x, E)$ in the exact formula (56).

The quantity of physical interest is W_n. To obtain W_n we expand the real part E_n in a power series in F, we expand the imaginary part $-\Gamma_n$ in $\exp(-2\beta/3F)$ times a power series in F, and we substitute these series into $\omega_n(E)$ (equation (79)) and $\mathscr{L}(E)$ (equation (82)) and then into equation (30). Then we collect terms of the same order in $\exp(-2\beta/3F)$. The equation for the real part of $\phi_n(x, W_n)$ becomes

$$[H^{(0)} - Fx + \mathscr{L}_{\mathrm{r}}(E_n) - \epsilon_n(W_n)]\phi_{n,\mathrm{r}}(x, W_n) \sim 0. \tag{90}$$

In fact, in equation (90), we have kept $\epsilon_n(W_n)$ (rather than $\epsilon_n(E_n)$) so that a comparison can be made with equation (87) with $E = E_n$ there. One sees that, neglecting terms of order $\exp(-2\beta/3F)$, $\epsilon_n(W_n)$ and $\phi_{n,\mathrm{r}}(x, W_n)$ satisfy the same equation as $\epsilon_n(E_n)$ and $\phi_{n,\mathrm{r}}(x, E_n)$. Another way to demonstrate this fact is provided by equation (63): $\epsilon_n(W_n)$ and $\epsilon_n(E_n)$ actually differ by $\mathrm{O}[\exp(-2\beta/3F)]$.

Consequently, the power series expansions for E_n and $\epsilon_n(E_n)$ must be identical:

$$E_n \sim \epsilon_n(E_n) \tag{91}$$

$$E_n^{(0)} = \epsilon_n^{(0)}(E_n^{(0)}) \tag{92}$$

$$E_n^{(1)} = \epsilon_n^{(1)}(E_n^{(0)}) + E_n^{(1)} \partial\epsilon_n^{(0)}(E_n^{(0)})/\partial E_n^{(0)} \tag{93}$$

and so forth.

But the system of equations for the asymptotic power series expansion of $\phi_{n,\mathrm{r}}(x, W_n)$ or $\phi_{n,\mathrm{r}}(x, E_n)$ (the two series are identical) and for E_n, equations (90)–(93), (77), (80), (83), (85) and (69)–(71), involve no imaginary quantities and are *precisely equivalent to the usual Rayleigh–Schrödinger treatment of the Stark effect.*

That is to say, since the equations solved are equivalent, the real parts of the outgoing-wave eigenfunction and energy have asymptotic power series that are

exactly those series obtained in the usual perturbation treatment of $H^{(0)} - Fx$, (which is a much more direct route for their calculation). Whenever $\phi_{n,r}(x, E_n)$ or $\phi_{n,r}(x, W_n)$ denotes a power series expansion, the reader may substitute the ordinary Rayleigh–Schrödinger series $\phi_{RS}(x)$ for the problem. With these series, an expansion for Γ_n can be obtained through equations (89) and (62). First we get

$$\Gamma_n = \frac{g_i(E_n)(\hbar^2/2m)\phi_{n,r}(a, E_n)^2}{\int_0^a \phi_{n,r}(x, E_n)^2 \, dx[1 - \mathrm{Re}\,\omega_n'(E_n)]} + O(\Gamma_n^2). \tag{94}$$

The denominator can be greatly simplified through equations (51)–(53) and some asymptotic sleight of hand:

$$\int_0^a \phi_{n,r}(x, E_n)^2 \, dx \, [1 - \mathrm{Re}\,\omega_n'(E_n)]$$

$$\sim \int_0^a \phi_{n,r}(x, E_n)^2 \, dx - \mathrm{Re}\,[(a + E_n/F) + \hbar^2 g^{(+)}(E_n)^2/2mF]\phi_{n,r}(a, E_n)^2 \tag{95}$$

$$\sim \int_0^\infty \phi_{n,r}(x, E_n)^2 \, dx. \tag{96}$$

The latter expression is to be interpreted as the integral of the square of the truncated perturbation series for $\phi_{n,r}(x, E_n)$. The justification lies in how equation (96) is used. To begin, any linear combination of Airy functions, such as $\mathscr{Ai}^{(+)}(-\xi)$, satisfies

$$\int_x^b \mathscr{Ai}^{(+)}(-\xi)^2 \, dx = \{(x + E/F)\mathscr{Ai}^{(+)}(-\xi)^2 + (\hbar^2/2mF)\,[(d/dx)\mathscr{Ai}^{(+)}(-\xi)]^2\}_x^b. \tag{97}$$

It is tempting to write

$$-(a + E_n/F) - \hbar^2 g^{(+)}(E_n)^2/2mF = \mathscr{Ai}^{(+)}(-\xi_a)^{-2} \int_a^\infty \mathscr{Ai}^{(+)}(-\xi)^2 \, dx \tag{98}$$

except that the integral does not converge. If, however, one first allows F to become small, then

$$\mathscr{Ai}^{(+)}(-\xi)/\mathscr{Ai}^{(+)}(-\xi_a) \sim \mathrm{Bi}(-\xi)/\mathrm{Bi}(-\xi_a) \qquad (\text{as } F \to 0) \tag{99}$$

and if the asymptotic expansion is truncated after a finite number of terms

$$\mathrm{Bi}(-\xi)/\mathrm{Bi}(-\xi_a) \sim \exp[\kappa(a - x)]\{1 + Fm\hbar^{-2}\kappa^{-3}[\tfrac{1}{2}\kappa(x - a) + \tfrac{1}{2}\kappa^2(x^2 - a^2)] + \ldots\} \tag{100}$$

then the integral does exist. Finally, since for $x \geqslant a$,

$$\phi_n(x, E_n)/\phi_n(a, E_n) = \mathscr{Ai}^{(+)}(-\xi)/\mathscr{Ai}^{(+)}(-\xi_a)$$

at least asymptotically, one ends up with equation (96). Although the argument has been somewhat heuristic, the result is correct as an asymptotic expansion. We note in passing, the obvious change in appearance that equation (96) gives to equation (47) for the evolution operator.

Next, following equation (68) for $g_i(E_n)$, we obtain final perturbation theory

derived formulae for Γ_n

$$\Gamma_n \sim (\hbar^2/2m)g_i(E_n)\phi_{n,r}(a, E_n)^2 \left(\int_0^\infty \phi_{n,r}(x, E_n)^2 \, dx \right)^{-1} \tag{101}$$

$$\sim \pi^{-1} F^{1/3} (\hbar^2/2m)^{2/3} \phi_{n,r}(a, E_n)^2 \left(\int_0^\infty \phi_{n,r}(x, E_n)^2 \, dx \, \mathrm{Bi}(-\xi_a)^2 \right)^{-1} \tag{102}$$

$$\sim (\hbar^2\kappa/2m)\phi_{n,r}(a, E)^2 \exp(2\kappa a) \exp(-2\kappa^3\hbar^2/3mF)$$

$$\times [1 - Fm\hbar^{-2}\kappa^{-3}(\tfrac{5}{12} + \kappa a + \kappa^2 a^2) + O(F^2)] \left(\int_0^\infty \phi_{n,r}(x, E_n)^2 \, dx \right)^{-1}. \tag{103}$$

It is to be emphasised that to use these formulae, the conventional perturbation expansions for E_n and $\phi_{n,r}$, and the conventional asymptotic expansion for $\mathrm{Bi}(-\xi_a)$, should be substituted into equations (101)–(103) and truncated to a consistent order in F.

The structure of equations (101)–(103) suggests a simple physical interpretation: the ionisation rate is a product of a system-independent factor, $\hbar g_i(E_{RS})/m$, and a system-dependent factor that represents the probability density at a point inside the barrier region but outside the range of the potential $V_0(x)$, $\psi_{RS}(a)^2 / \int_0^\infty \psi_{RS}(x)^2 \, dx$. The probability density is evaluated from the usual Rayleigh–Schrödinger perturbation expression, $\psi_{RS}(x)$. (Strictly speaking, $g_i(E_{RS})$ is not entirely system-independent, in that it is evaluated at the 'perturbed energy' E_{RS}.)

4. Alternative approaches for calculating the complex eigenvalues

In the preceding section a perturbation theory based on small F asymptotic expansions was developed for calculating the Kapur–Peierls eigenvalues $\omega_n(E)$ and the 'outgoing-wave eigenvalues' W_n. In this section we briefly sketch two alternative approaches, one based on perturbation theory, the second on a formula of Lagrange.

Let us take only real values of E. Further let us partition $\mathscr{H}$ so that the imaginary part of $\mathscr{L}$ is regarded as the perturbation:

$$\mathscr{H}^{(0)} = H^{(0)} - Fx + \mathscr{L}_r \tag{104}$$

$$\mathscr{V} = i\mathscr{L}_i. \tag{105}$$

The Hamiltonian $\mathscr{H}^{(0)}$ is Hermitian on $[0, a]$, and if we may borrow the notation of the preceding section, let us assume that its eigenfunctions and eigenvalues are known:

$$\mathscr{H}^{(0)}\phi_{n,r}(x, E) = \epsilon_n(E)\phi_{n,r}(x, E). \tag{106}$$

Both the eigenvalues and eigenfunctions are real. Hereafter we use $\epsilon_n(E)$ to denote the eigenvalue of $\mathscr{H}^{(0)}$, not $\mathrm{Re}\,\omega(E)$ as in equation (79). Standard Rayleigh–Schrödinger perturbation theory applied to $\mathscr{H}^{(0)} + \mathscr{V}$, with care taken with the non-Hermiticity of the perturbation, yields very simple expressions because of the simplicity of the matrix elements,

$$\int_0^a \phi_{m,r}(x, E)\mathscr{L}_i\phi_{n,r}(x, E) \, dx = -(\hbar^2/2m)g_i(E)\phi_{m,r}(a, E)\phi_{n,r}(a, E). \tag{107}$$

In such a manner one may obtain

$$\omega_n(E) = \epsilon_n(E) - \mathrm{i}(\hbar^2/2m)g_\mathrm{i}(E)\frac{\phi_{n,\mathrm{r}}(a,E)^2}{N_{n,\mathrm{r}}(E)} + \sum_{\substack{m \\ (m\neq n)}} (\hbar^2/2m)^2 \frac{g_\mathrm{i}(E)^2\phi_{n,\mathrm{r}}(a,E)^2\phi_{m,\mathrm{r}}(a,E)^2}{[\epsilon_m(E)-\epsilon_n(E)]N_{n,\mathrm{r}}(E)N_{m,\mathrm{r}}(E)} + \mathrm{O}(g_\mathrm{i}^3) \tag{108}$$

$$\phi_n(x,E) = \phi_{n,\mathrm{r}}(x,E) - \sum_{\substack{m \\ (m\neq n)}} (-\mathrm{i})g_\mathrm{i}(E)\phi_{m,\mathrm{r}}(x,E)\frac{\phi_{m,\mathrm{r}}(a,E)\phi_{n,\mathrm{r}}(a,E)}{[\epsilon_m(E)-\epsilon_n(E)]N_{m,\mathrm{r}}(E)} + \mathrm{O}(g_\mathrm{i}^2). \tag{109}$$

Here, $N_{n,\mathrm{r}}(E)$ denotes the normalisation integral

$$N_{n,\mathrm{r}}(E) = \int_0^a \phi_{n,\mathrm{r}}(x,E)^2\,\mathrm{d}x. \tag{110}$$

To obtain W_n, we further develop the approach by taking as the perturbation not equation (105), but

$$\begin{aligned}\mathscr{V} &= \mathscr{L}(W_n) - \mathscr{L}_\mathrm{r}(E)\\ &= \mathscr{L}_\mathrm{r}(W_n) - \mathscr{L}_\mathrm{r}(E) + \mathrm{i}\mathscr{L}_\mathrm{i}(W_n)\\ &= (\hbar^2/2m)\delta(x-a)[g_\mathrm{r}(E) - g_\mathrm{r}(W_n)] - \mathrm{i}(\hbar^2/2m)\delta(x-a)g_\mathrm{i}(W_n).\end{aligned} \tag{111}$$

In the resulting Rayleigh–Schrödinger series for $\omega_n(W_n)$, W_n appears both on the left $[W_n = \omega_n(W_n)]$ and on the right in $\mathscr{V}$. Its value must be obtained self-consistently. Towards this end one expands $\mathscr{V}$ in $W_n - E$:

$$\mathscr{V} = \mathrm{i}\mathscr{L}_\mathrm{i}(E) - (\hbar^2/2m)\delta(x-a)\sum_{l=1}^{\infty}(W_n-E)^l(l!)^{-1}(\mathrm{d}/\mathrm{d}E)^l g^{(+)}(E). \tag{112}$$

Then one obtains the expansion

$$\begin{aligned}W_n - E &= \omega_n(W_n) - E\\ &= \epsilon_n(E) - E - \mathrm{i}(\hbar^2/2m)g_\mathrm{i}(E)\phi_{n,\mathrm{r}}(a,E)^2/N_{n,\mathrm{r}}(E)\\ &\quad - (\hbar^2/2m)(W_n-E)(\mathrm{d}/\mathrm{d}E)g^{(+)}(E)\phi_{n,\mathrm{r}}(a,E)^2/N_{n,\mathrm{r}}(E)\\ &\quad - (\hbar^2/2m)(W_n-E)^2\tfrac{1}{2}(\mathrm{d}/\mathrm{d}E)^2 g^{(+)}(E)\phi_{n,\mathrm{r}}(a,E)^2/N_{n,\mathrm{r}}(E)\\ &\quad - \sum_{\substack{m \\ (m\neq n)}} \frac{(\hbar^2/2m)^2[-\mathrm{i}g_\mathrm{i}(E) - (W_n-E)\,\mathrm{d}g^{(+)}(E)/\mathrm{d}E]^2}{[\epsilon_m(E)-\epsilon_n(E)]N_{n,\mathrm{r}}(E)N_{m,\mathrm{r}}(E)}\\ &\quad \times \phi_{n,\mathrm{r}}(a,E)^2\phi_{m,\mathrm{r}}(a,E)^2 + \mathrm{O}[(W_n-E)^3] + \mathrm{O}[(W_n-E)^2 g_\mathrm{i}(E)].\end{aligned} \tag{113}$$

Solving for $W_n - E$ through first order, one obtains

$$\begin{aligned}W_n - E &= [\omega_n(E) - E]/[1 + (\hbar^2/2m)(\mathrm{d}/\mathrm{d}E)g^{(+)}(E)\phi_{n,\mathrm{r}}(a,E)^2/N_{n,\mathrm{r}}(E)]\\ &\quad + \mathrm{O}[(W_n-E)^2] + \mathrm{O}[g_\mathrm{i}(E)(W_n-E)]\end{aligned} \tag{114}$$

where $\omega_n(E)$ has already been given by equation (108).

We notice that if E is chosen to be $\tilde{E}_n$, the solution of

$$\tilde{E}_n = \epsilon_n(\tilde{E}_n), \tag{115}$$

then the real part of $W_n - E$ is second order in g_i. This result is to be expected, because if one were to apply the perturbation theory of the preceding section, it is clear from equation (91) that E_n (the real part of W_n) and $\tilde{E}_n$ have the same asymptotic power series in F (cf also equation (63)).

The implication is that the appropriate value to use in equations (111)–(114) is $\tilde{E}_n$. Such a choice also simplifies the self-iteration of equation (113) to eliminate higher powers of $W_n - E$. Thus equations (113) and (114) become

$$-\operatorname{Im}(W_n - \tilde{E}_n) = \frac{(\hbar^2/2m)g_i(\tilde{E}_n)\phi_{n,r}(a, \tilde{E}_n)^2}{N_{n,r}(\tilde{E}_n)[1 + (\hbar^2/2m)(d/d\tilde{E}_n)g_r(\tilde{E}_n)\phi_{n,r}(a, \tilde{E}_n)^2/N_{n,r}(\tilde{E}_n)]} + O[g_i(\tilde{E}_n)^3] \tag{116}$$

$$\operatorname{Re}(W_n - \tilde{E}_n) = \left[\frac{\operatorname{Im}(W_n - \tilde{E}_n)(\hbar^2/2m)[dg_i(\tilde{E}_n)/d\tilde{E}_n]\phi_{n,r}(a, \tilde{E}_n)^2}{N_{n,r}(\tilde{E}_n)} + [\operatorname{Im}(W_n - \tilde{E}_n)]^2 \left(\frac{(\hbar^2/2m)\frac{1}{2}(d/d\tilde{E}_n)^2 g_r(\tilde{E}_n)\phi_{n,r}(a, \tilde{E}_n)^2}{N_{n,r}(\tilde{E}_n)} + \sum_{\substack{m \\ (m \neq n)}} \frac{N_{n,r}(\tilde{E}_n)\phi_{m,r}(a, \tilde{E}_n)^2/\phi_{n,r}(a, \tilde{E}_n)^2}{[\epsilon_m(\tilde{E}_n) - \epsilon_n(\tilde{E}_n)]N_{m,r}(\tilde{E}_n)} \right) \right] \times [1 + (\hbar^2/2m)(d/d\tilde{E}_n)g_r(\tilde{E}_n)\phi_{n,r}(a, \tilde{E}_n)^2/N_{n,r}(\tilde{E}_n)]^{-1} + O[g_i(\tilde{E}_n)^3]. \tag{117}$$

Equation (116) should be compared with equations (94), (89), and (62).

We conclude this section by suggesting another formula for the calculation of W_n. We suppose that the Kapur–Peierls eigenvalue $\omega_n(E)$ and its derivatives be determined for E at a point near W_n. We may take E to be real. The value of W_n may be determined (provided that the series converges) by a formula due to Lagrange, which has been used in perturbation theory by des Cloizeaux (1960), Sack (preprint) and Silverstone and Holloway (1970, 1971):

$$W_n = E + \sum_{l=1}^{\infty} (l!)^{-1}(d/dz)^{l-1}[\omega_n(z) - E]_{z=E}^{l}. \tag{118}$$

We note that equations (94) and (116) can be obtained from the Lagrange expansion above by omitting all derivatives of $\omega_n(z)$ higher than the first, by summing the remaining geometric series, and then by choosing the appropriate value of E.

5. Square-well example

As an illustration, we consider a square-well potential: $V_0(x) = -U_0$ for $(0 \leqslant x \leqslant a)$, and $V_0(x) = 0$ for $(x \geqslant a)$. To make the computational details even simpler, we apply the external field only in the exterior region. This model is in the spirit of Duke and Alferieff (1966). In the interior region the Kapur–Peierls eigenfunctions

are just $\sin(K_n x)$, with

$$K_n = \{(2m/\hbar^2)[U_0 + \omega_n(E)]\}^{1/2}. \tag{119}$$

The K_n, and hence the $\omega_n(E)$, can be determined exactly from the matching condition

$$K_n \cot(K_n a) = g^{(+)}(E) \tag{120}$$

and the W_n from the simultaneous solution of equation (120) (with E replaced by W_n) and

$$W_n = (\hbar^2/2m)K_n^2 - U_0. \tag{121}$$

Numerical results of such a calculation appear in table 1 for fairly high field strengths ($F = 0{\cdot}3$ to $0{\cdot}5$ au). We have chosen high field strengths for a better test of the perturbation results. For the values of ξ_a that occur, the $\mathrm{Ai}(-\xi_a)$ and $\mathrm{Bi}(-\xi_a)$ appearing in $g^{(+)}(E)$ can be evaluated by power series, and W_n can be obtained by iterating $W_n = \omega_n(W_n)$. The parameters a and U_0 have been chosen so that $V_0(x)$ supports a single bound state at $E = -2$ au (1 au $\simeq$ 27·2 eV), and the subscript $n = 0$ in table 1 indicates continuity with that level. Note how insensitive the real part of the KP eigenvalue is to E, and how very sensitive the imaginary part is.

We may also calculate the quantities of table 1 by perturbation theory. It is not too difficult, but somewhat tedious, to generate the Rayleigh–Schrödinger expansions as discussed in §3. Because of the high field strengths, several terms would be needed. A more efficient route, made practical by the simplicity of the square-well potential, is to solve directly for the entire asymptotic real part of the perturbed KP eigenvalue and eigenfunction, as given by equation (106). The

Table 1. (*a*) Kapur–Peierls and (*b*) 'outgoing-wave' (Siegert) energies for a square-well potential of depth $U_0 = 2{\cdot}82589$ (for $0 \leqslant x \leqslant a = 2{\cdot}0$) with a strong electric field outside a, $-Fx$ ($a \leqslant x$). The U_0 and a are given in atomic units ($\sim$ 27·2 eV and 0·53 Å). The values of U_0 and a have been chosen so that when F vanishes, there is a bound state at energy $-2{\cdot}0$.

(*a*) The Kapur–Peierls ground-state energy as a function of E for F fixed at 0·4.

E	$\mathrm{Re}\,\omega_0(E)$	$-\mathrm{Im}\,\omega_0(E)$
−1·0	−2·2993	0·1317
−1·5	−2·1737	0·0152
−2·0	−2·0811	0·000515
−2·0720	−2·0720	0·000293
−2·5	−2·0293	0·00000732
−3·0	−1·9940	0·0000000518

(*b*) Outgoing-wave (Siegert) energy as a function of field strength.

F	$E_0 = \mathrm{Re}\,W_0$	$\Gamma_0 = -\mathrm{Im}\,W_0$
0·5	−2·1017	0·002762
0·4	−2·0720	0·000261
0·3	−2·0489	0·00000400

Table 2. Eigenvalues by perturbation theory (in au).

(*a*) Energy-dependent real Kapur–Peierls eigenvalues obtained from the real part of the Kapur–Peierls boundary condition, corresponding to the infinite-order Rayleigh–Schrödinger result, along with imaginary corrections, for F fixed at 0·4.

E	$\epsilon_0(E)$[a]	$-\gamma_0(E)$[b]
−1·0	−2·3193	0·1341
−1·5	−2·1740	0·0152
−2·0	−2·0811	0·000515
−2·5	−2·0293	0·00000732
−3·0	−1·9940	0·0000000518

(*b*) Perturbed energy, obtained by solving $\tilde{E}_0 = \epsilon_0(\tilde{E}_0)$, and corresponding to the infinite-order Rayleigh–Schrödinger result, along with the imaginary correction.

F	$\tilde{E}_0$[c]	$\tilde{\Gamma}_0 = -\mathrm{Im}\,(W_0 - \tilde{E}_0)$[d]
0·5	−2·1016	0·002783
0·4	−2·0720	0·000261
0·3	−2·0489	0·00000400

[a] See equation (106) of text.
[b] See equation (89) of text.
[c] See equation (115) of text.
[d] See equation (116) of text.

imaginary part of the eigenvalue is then given by equation (89) or the imaginary term in equation (108). Note that the explicit form of $\phi_{n,\mathrm{r}}(a, E) = \sin(K_n a)$ in equation (89) yields

$$\gamma_n(E) \sim -g_{\mathrm{i}}(E)(\hbar^2/2m)/\{\tfrac{1}{2}a[\cot^2(K_n a) + 1] - (2K_n)^{-1}\cot(K_n a)\}\,. \quad (122)$$

The $\epsilon_0(E)$ and $\gamma_0(E)$ so obtained are reported in the first part of table 2. The agreement with table 1 is remarkable.

In the same spirit, we obtain a perturbed energy $\tilde{E}_n$ directly by obtaining a self-consistent solution of equation (115), rather than through the series expansion. Practically, the calculation is to solve equations (120) and (121) simultaneously, but with $g^{(+)}(E)$ replaced by $g_{\mathrm{r}}(\tilde{E}_n)$. Then the imaginary part of W_n is obtained from equations (116) and (122). The results are given in the lower part of table 2, and the agreement with the exact results of table 1 are quite good.

In this paper we have developed the mathematical background for treating resonant states in a uniform electrostatic field. The actual system of atomic hydrogen will be discussed elsewhere in a subsequent paper (Yamabe *et al* 1977).

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