cross section with a value of $\sigma_r = (1.0 \pm 0.15) \times 10^{-15}$ cm^2 was determined for the resonant-transfer collision process between the He 2^1S metastable level and the Ne $3s_2$ level.

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Two Electrons in a Coulomb Potential. Double-Continuum Wave Functions and Threshold Law for Electron-Atom Ionization*†

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The Schrödinger equation for two electrons in a Coulomb field is studied in the critical region where both electrons have near-zero kinetic energies. The main feature of this problem is that the mutual screening between the two electrons determines and is determined by the partition of the available energy between them. This energy-dependent screening can be taken into account to yield a complex potential in the radial variable $R = (r_1^2 + r_2^2)^{1/2}$ of the six-dimensional configuration space of the two electrons. Solutions of this equation are obtained and are shown to correspond to the classical orbits given in an early paper by Wannier. A possible way is indicated of using these wave functions to establish the Wannier threshold law which, for ionization of neutral atoms, is $\sigma \propto E^{1.127}$. Finally, the interplay between the total energy and the Coulomb potential is discussed both for this problem and for the case of one electron in the field of a nucleus.

I. INTRODUCTION

The increasing attention being given, in both experimental and theoretical atomic physics, to correlation effects between electrons makes the prototype system of two electrons in the field of a nucleus of increasing conceptual and practical interest. The correlation effects are expected to be especially significant when the two electrons have near-zero energies. This is a situation that obtains in the classic three-body problem of the threshold behavior of the cross section for ionization of atoms by electron impact.[1] As we will see, a crucial feature of the two-electron continuum wave functions near threshold is that they include a large number of spherical harmonics of *either* electron,[2] even when the *total* wave function is restricted to an S state. The divergence of this number distinguishes the ionization threshold from the threshold for excitation of any level that lies below the ionization limit by a finite amount. Arguments for a linear threshold law for ionization on the basis of extrapolation from excited states are invalidated by this feature, which puts the ionization threshold on a *qualitatively* different footing. The same divergence in l values is of practical interest because it represents a long-range correlation which will be important for electron-atom scattering calculations at energies approaching the ionization limit from *either* direction. The influence of this effect has already been felt in close-coupling calculations of collision processes, which agree quite well with experiment when the energy is near the $n = 2$ or 3 levels and again when the energy is appreciably above the ionization limit, but depart very significantly from experiment in the intermediate range. The two-electron wave functions derived in this paper emphasize precisely this long-range angular correlation which has so far not been included in any calculation. Analogous effects should occur, of course, near the threshold for breakup into a still larger number of particles and may be analyzed along similar lines.

The threshold law for the ionization of atoms by electrons was first considered by Wannier,[1] who, in an elegant treatment of Hamilton's classical equations of motion and of the phase space relevant to ionization, established a threshold law which takes into account the "dynamic" or energy-dependent screening of one electron by the other. This work seems very convincing to us and we can only attribute the hesitation of many in accepting his results to the fact that it is a classical and not quantum-mechanical treatment. Some progress towards extension of the classical analysis has been made by Peterkop and Liepinsh,[3] who carried out the WKB treatment of a simplified problem (the electrons are taken to be in one dimension) and also arrived at Wannier's result. The study of the two-electron Schrödinger equation that we attempt in this paper is guided strongly by the lines Wannier's argument takes.

The arrangement of the paper is as follows. The main treatment begins in Sec. III with a qualitative discussion of the principal features of the electron-electron interaction. However, as a preliminary, Sec. II discusses aspects of alternative normalizations of continuum wave functions, particularly with a Coulomb potential, indicating their connection to threshold laws and particularly emphasizing assumptions which have led to different proposals for the threshold law for electron-atom ionization. This serves to motivate the features emphasized in Sec. III and further is important for considerations of the normalization of the two-electron wave functions that we derive in Sec. V. Section IV considers the solution of the two-electron equation to arrive at zero-energy wave functions which incorporate the ideas of Sec. III; a way of arriving at the Wannier threshold law starting from these zero-energy wave functions is then considered in Sec. V. The main thread of solutions of the two-electron equation is again taken up in Sec. VI, where solutions that are more general than those in Sec. IV are derived. This brings out the connection of zero-energy wave functions with those at finite energy and also the role of various regions of space in problems with a Coulomb potential; the Appendix discusses mathematical aspects of the connection between these regions and the alternative expansions of the Coulomb wave function relevant to them.

II. PHASE SPACE, CONTINUUM NORMALIZATION, AND THRESHOLD LAWS

The problem of the threshold behavior of processes involving scattering from potential wells and two-particle scattering dates back to a 1948 paper by Wigner.[4] He emphasized the crucial feature that the threshold behavior is a feature of the escape process and does not involve details of what goes on in the "reaction zone" where the particles are close together and interact strongly. This has an important implication which we will exploit, namely, that threshold laws can be worked out even in the absence of a full quantum-mechanical solution in the reaction zone, which is usually the most complicated region of the problem. Further, the physical significance of the Wigner argument is that the way the "initial complex" is prepared in the reaction zone is irrelevant for the threshold law. For our problem this implies that the threshold law for electron-atom ionization is the same as that for double ionization of an atom by a single photon.

The energy dependence of the cross section for an inelastic process enters through the phase-space factor and through the wave functions according to

$$\sigma = (\text{phase space}) \times \left| (\psi_f, V_f \Psi_i^+) \right|^2 , \tag{1}$$

where the wave functions are normalized per unit volume. ψ_f is the unperturbed final-state wave function, V_f the perturbation in the final channel, and Ψ_i^+ is the exact wave function which includes the incident wave and outgoing scattered wave. Various alternative forms may be used for the transition matrix element in Eq. (1); for example, $(\Psi_f^-, V_i \psi_i)$, where the minus indicates that an ingoing scattered wave is included. For the purpose of deriving threshold laws, however, these complexities are not relevant because it is well known[5] that the Born approximation form of the matrix element in which only unperturbed wave functions enter is adequate. But it must be emphasized that we must use the correct forms for these wave functions, which requires that for the electron-atom ionization problem, ψ_f must be solutions of the full three-body equation. We will shortly see that so far all attempts to derive the threshold law have used instead a product of wave functions for each electron and not true two-electron functions.

But first let us consider the phase-space factor which is necessary when one adopts normalization per unit volume. When a single electron leaves the reaction zone, this factor is $k_f^2(dk_f/dE)$ and hence equal to k_f because $E = \frac{1}{2}k_f^2$, where E is the energy available in the final channel (we use a.u. throughout). Explicit use of this factor could be avoided by using wave functions normalized per unit energy range. We choose, however, to work with functions normalized per unit volume and keep the phase space separate, partly because this factor has its own physical significance and it is useful to display its influence separated from the specific dynamics of the process. Further,

we shall in later sections consider wave functions in six-dimensional space; normalization per unit volume takes the dimensionality of space into account more readily. For ordinary three-dimensional wave functions, the various normalizations are connected by the rule

(functions normalized per unit momentum)

$= k$(functions normalized per unit volume)

$= k^{1/2}$(functions normalized per unit energy).

This rule expresses how the terms in the phase-space factor, $k^2(dk/dE)$, are successively taken into account in going from normalization per unit volume to that for unit energy. Wave functions with a short-range potential with these three alternative normalizations (per unit momentum, per unit volume, and per unit energy) are, respectively, $kj_l(kr)$, $j_l(kr)$, and $k^{1/2}j_l(kr)$. The second of these, when combined with the knowledge that $j_l(kr) \propto (kr)^l$ as $k \to 0$, gives the Wigner result through Eq. (1), $\sigma \propto k_f^{2l+1}$, for excitation thresholds when there is no long-range interaction in the final channel. Notice that phase space alone contributes the factor k_f or $E^{1/2}$. S-wave thresholds display this characteristic square-root behavior.

If there is a Coulomb potential in the final channel, the radial wave function $R_f(kr) = P_f(kr)/kr$ obeys[6] the equation

$$\left(\frac{d^2}{d(kr)^2} + 1 + \frac{\frac{1}{4} - (l+\frac{1}{2})^2}{(kr)^2} - \frac{2\eta}{kr} \right) P_f(kr) = 0 \ , \tag{2}$$

where $\eta = Z/k$ and is negative for an attractive potential. The regular solution, normalized per unit volume, is

$$P_f(kr) \propto e^{-\pi\eta/2} \left| \Gamma(l+1+i\eta) \right| (kr)^{l+1} e^{-ikr} \times M(l+1-i\eta, 2l+2, 2ikr) \ ,$$

which reduces to the zero-energy form $P_f(kr) = (kr)^{1/2} J_{2l+1}[(8Zr)^{1/2}]$. Zero-energy solutions, normalized per unit energy, then turn out to be[7] $R_f(kr) = r^{-1/2} J_{2l+1}[(8Zr)^{1/2}]$ and hence independent of energy. It is clear from these energy dependences that Eq. (1) now yields a constant threshold law for the cross sections when there is a Coulomb potential in the final channel, which is a well-known result.

The volume normalization admits immediate generalization to N-dimensional Coulomb functions. The transformation $R_f(kr) = P_f(kr) \times (kr)^{-(N-1)/2}$ leads always to Eq. (2) for $P_f(kr)$, which may, therefore, be considered to be the equation for one-dimensional Coulomb functions. Thus N-dimensional Coulomb functions, normalized per unit volume, have the k dependence near threshold given by $R_f(kr) \propto k^{-(N-2)/2}$.

Let us now consider some three-body threshold laws. Since we have two particles leaving the reaction zone, the phase-space volume element is proportional to $\kappa_1^2(d\kappa_1/dE_1)\kappa_2^2(d\kappa_2/dE_2)$, where κ_1 and κ_2 are the two wave numbers. With the condition $E = \frac{1}{2}(\kappa_1^2 + \kappa_2^2) = E_1 + E_2$ we have to integrate over all possible energy partitions between the two electrons. The double integral $\int\int dE_1 dE_2 \times \delta(E - E_1 - E_2)$ reduces to an integral over the energy of just one electron. We have finally

$$\sigma = \int_0^k \kappa_1^2 \kappa_2 d\kappa_1 \left| \text{matrix element} \right|^2 \ , \tag{3}$$

where $E = \frac{1}{2}k^2$.

Several results now follow from Eq. (3) and we wish to focus on these as a background for later results in this paper:

(a) If the matrix element brings in no energy dependence (recall that we have to use wave functions normalized per unit volume), then Eq. (3) gives $\sigma \propto E^2$, a result given by Delves[8] for deuteron breakup by neutrons. Note that this is just a phase-space factor.

(b) In the context of atomic physics, when two electrons leave a positive ion, there has been no unequivocal derivation of the threshold law. This is because so far there has been no unambiguous form for the wave function of the final state and various authors have made various assumptions[9] for this form. One form, in which one electron is assumed to screen the nuclear potential completely, takes for the final state a product of a Coulomb wave for this electron and a plane wave for the other. Hence, $P_f \propto \kappa_1^{1/2}$ or $\kappa_2^{1/2}$. Either of these gives through Eq. (3) the result $\sigma \propto E^{3/2}$. An alternative assumption, that both electrons can be represented by Coulomb waves, gives $P_f \propto (\kappa_1\kappa_2)^{1/2}$ and hence $\sigma \propto E$; this law would follow, for instance, if neither electron screens the field for the other. Note also that if we wrote a joint wave function for the two electrons as a six-dimensional Coulomb wave, we know from the earlier discussion that $R_f \propto k^{-2}$ and hence $\sigma \to$ const, a result noted earlier by Peterkop.[10] No one of these results can be accepted as the correct threshold law; as pointed out earlier, we have to use in Eq. (3) a final-state wave function that is a solution of the full two-electron Schrödinger equation. It is these solutions that we derive in the next sections.

Summarizing, we can see through consideration of phase space and normalization factors the assumptions which underlie different proposals for the electron-atom ionization threshold law. The main result to bear in mind in later sections is that assuming no screening gives a linear law whereas the opposite extreme of full screening

gives the $E^{3/2}$ law.

III. DYNAMIC SCREENING AND WANNIER ORBITS

In the ionization of an atom by an incident electron, the main feature of the outgoing configuration is the interaction of one electron with the other—a mutual screening effect. The last paragraphs of Sec. II have emphasized that for threshold behavior this effect must be properly treated. In a time-dependent framework the escape process may be viewed as follows. As the electrons move away from the nucleus, the way in which the total available energy is partitioned into the kinetic energies of the electrons will determine their velocities and hence their distances from the nucleus. If we consider the system as an electron in a screened Coulomb field due to the nucleus and the other electron, then we will have one such configuration at any one instant of time (or, alternatively, at any one value of distance parameter R which will be introduced later). The configuration at any instant will in turn determine the subsequent energy exchange between the two electrons which will, of course, lead to new values of the relative distances of the electrons and hence to a new configuration. Thus there will be a sequence of such configurations in time, representing the escape process. This phenomenon, which we call "dynamic screening," plays a particularly significant role near threshold because the electrons are slow and if one gains energy at the expense of the other, the latter may be prevented from escaping. This dynamic screening has been considered only in the work of Wannier, [1] who solved the classical equations of motion in a restricted region of configuration space which is relevant to this critical interaction between two slow electrons. He derived a threshold law with a Z-dependent exponent which lies between 1 and $\frac{3}{2}$. Section II has made plausible the supposition that the exponent will lie between 1 and $\frac{3}{2}$. The remarks on dynamic screening make clear that the escape process is a continuous competition between the nuclear attraction and the interelectronic repulsion. The former is Z dependent and the latter is not; hence the decreasing effect of dynamic screening as Z increases makes the appearance of a Z dependence in the threshold law quite natural. In fact, the exponent in the Wannier threshold law decreases towards 1 as Z increases, which is just what we would expect.

The phenomenon of dynamic screening has been described in the last paragraph in a time-dependent or perturbative framework. There will, of course, be a time-independent or stationary-state picture, which we adopt in the rest of this paper. This is particularly suitable near threshold because the two electrons have about equal energy and it is artificial to single out one to give a screened Coulomb field for the other. It is much more natural to treat the whole complex of nucleus and two electrons as a single system. This is suitably done by using hyperspherical coordinates:

$$R=(r_1^2+r_2^2)^{1/2}\,,\quad \tan\alpha=r_2/r_1\,,$$

and

$$\vartheta_{12}=\arccos\hat{r}_1\cdot\hat{r}_2\,,$$

where $\vec{r}_1, \vec{r}_2$ are the radius vectors of the electrons from a center of charge $+Ze$. We further restrict ourselves to $L=0$ [11] (total angular momentum of the two electrons). With this choice, a coordinate set $(R, \alpha, \vartheta_{12})$ defines the location of a configuration point of the whole system. The mutual positions of the two electrons are now given by the values of α and ϑ_{12}, where the former, a pseudoangle, represents radial correlation and the latter, angular correlation. The effect and importance of dynamic screening translates in these terms into the effect and importance of the (α, ϑ_{12}) part of the Schrödinger equation on the remainder of the equation in R. This process of converting the two-electron problem into one of the motion of a point in a six-dimensional space could, of course, be generalized to more particles.

Wannier argued that near threshold the region relevant to ionization is one in which the two electrons recede from the vicinity of the nucleus in opposite directions, $\vartheta_{12}\simeq\pi$, and with nearly equal velocities, i.e., $r_1\simeq r_2$ or $\alpha\simeq\frac{1}{4}\pi$. The first is plausible because the $1/r_{12}$ repulsion acting between the two slow electrons would tend to push their radii vectors apart. Further, this has an important physical significance. Even when L, the total angular momentum, is zero there is no restriction on the magnitudes of the l values of the individual electrons so long as they are equal. In fact, the tight correlation $\vartheta_{12}\simeq\pi$ demands that there be a superposition of a large number of spherical harmonics. As remarked in the Introduction, this large multiplicity, infinite in the limit of threshold, is what distinguishes the ionization threshold from those that involve a finite excitation. It is interesting that the presence of several l values near threshold is apparent in angular correlation experiments [12] of $e+\mathrm{He}$ ionization which show that there is still structure in the angular differential cross section several eV above threshold.

The second condition, $\alpha\simeq\frac{1}{4}\pi$, is a consequence of dynamic screening. If instead of having equal energies, one electron gets a little faster, then the other lags behind, screens the nuclear field more, and thus enhances the discrepancy in the energies. Thus the slower electron will be progressively slowed down and finally prevented from

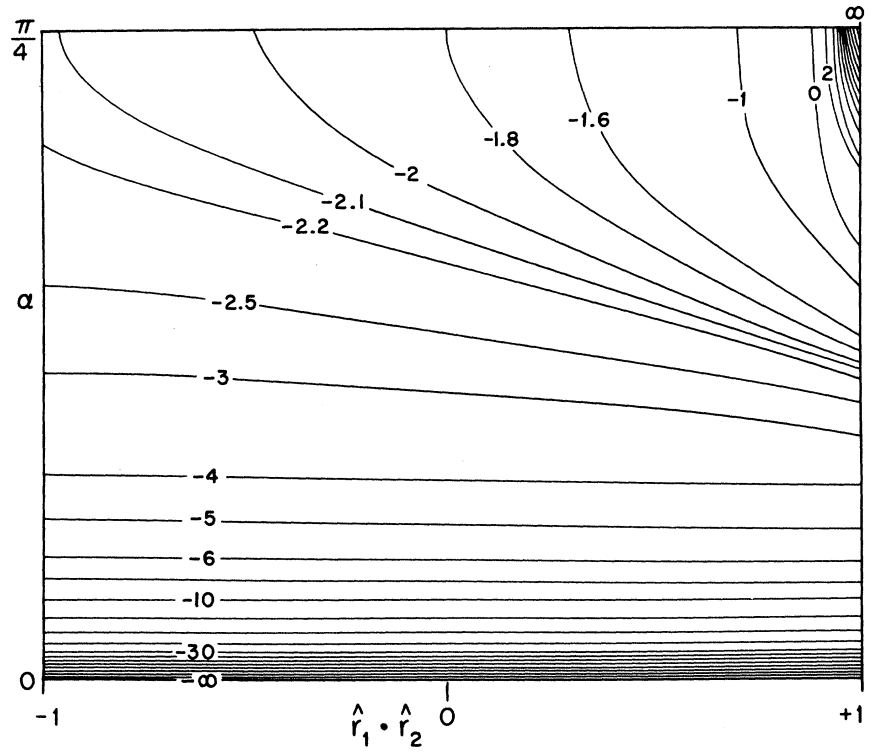

FIG. 1. Sketch of $e+\mathrm{H}$ potential $-B(\alpha,\vartheta_{12})$ in hyperspherical coordinates. Numerical entries give potential energy in a.u. for $R=1$ a.u.

escaping. In terms of a configuration point in hyperspace, $\alpha \simeq \frac{1}{4}\pi$ represents a ridge of the potential; the above remark indicates that wave-front propagation along this ridge is unstable (see Fig. 1).

With these arguments, the "direction" $\alpha \simeq \frac{1}{4}\pi$, $\vartheta_{12} \simeq \pi$ is seen to be the one leading to double escape near threshold. Wannier solved the classical equations of motion in this region by calculating a trajectory of the system represented by $\alpha(R)$ and $\vartheta_{12}(R)$. He found

$$\alpha - \tfrac{1}{4}\pi = e^{-q/4}(C_1 e^{-\mu q/2} + C_2 e^{\mu q/2}) \ ,$$

$$\vartheta_{12} - \pi = C_3 e^{-q/4} \cos(\tfrac{1}{2}\rho q + C_4) \ ,$$

where $q = \ln(R/b)$, where b is a const $\simeq$ 2 a.u., C_i are arbitrary constants, and

$$\mu = \frac{1}{2}\left(\frac{100Z-9}{4Z-1}\right)^{1/2} \ , \quad \rho = \frac{1}{2}\left(\frac{9-4Z}{4Z-1}\right)^{1/2} .$$

These Wannier orbits with the alternative values $+\mu$ and $-\mu$ correspond to two patterns of orbits in α, one converging to and one diverging from $\alpha = \frac{1}{4}\pi$ as $R \to \infty$. The first pattern always leads to ionization because it reaches $\alpha = \frac{1}{4}\pi$ at $R = \infty$, i.e., $r_1 = r_2 = \infty$. However, another feature in the Wannier theory has the consequence that at any finite energy, the diverging orbits can also lead to double escape. This is because the above orbits only extend up to a value of R given by $\simeq 2Zk^{-2}$, beyond which they are not valid. But in this "far zone" the potential is negligible compared to the total energy $\frac{1}{2}k^2$ and the electrons are essentially free, so that any orbits which reach this boundary around the Wannier direction $\alpha \simeq \frac{1}{4}\pi$, $\vartheta_{12} \simeq \pi$ will lead to ionization. Thus there will be some diverging orbits giving double escape at finite k. Wannier argued that at any finite energy, the converging orbits form a set of measure zero compared to the diverging ones and hence the threshold behavior is determined by the energy dependence of the diverging pattern, i.e., by the energy dependence of the coefficient C_2. Wannier established this dependence through statistical arguments and arrived at the threshold law $\sigma \propto E^{\mu/2-1/4}$. For neutral atoms, $Z=1$, this gives $\sigma \propto E^{1.127}$. Note that for $Z=\infty$, the exponent reduces to 1, as one would expect from the result of Sec. II that "no screening" leads to a linear law.

IV. ZERO-ENERGY WAVE FUNCTIONS CORRESPONDING TO WANNIER'S ORBITS

In this section we look for the quantum-mechanical realization of the classical results presented in Sec. III. We will see that zero-energy wave functions near threshold incorporate all the features that the classical solutions exhibit and in Sec. V we will argue that these functions may be used to derive the threshold law.

Thus, with Sec. III in mind, let us look for solutions of the two-electron Schrödinger equation along the Wannier direction. The wave function for $L=0$ can be written as

$$\Psi(r,\alpha,\vartheta_{12}) = R^{-5/2}\csc 2\alpha\,\phi(R,\alpha,\vartheta_{12})\,, \tag{4a}$$

where ϕ satisfies

$$\left[\frac{\partial^2}{\partial R^2} + \frac{\frac{1}{4}}{R^2} + k^2 + \frac{1}{R^2}\frac{\partial^2}{\partial\alpha^2} + \frac{4}{R^2\sin^2 2\alpha}\,\frac{1}{\sin\vartheta_{12}} \times \frac{\partial}{\partial\vartheta_{12}}\left(\sin\vartheta_{12}\frac{\partial}{\partial\vartheta_{12}}\right) + \frac{2ZB(\alpha,\vartheta_{12})}{R}\right] \times \phi(R,\alpha,\vartheta_{12}) = 0\,, \tag{4b}$$

$\frac{1}{2}k^2$ is the total energy, and $-ZB(\alpha,\vartheta_{12})/R$ is the potential with

$$B(\alpha,\vartheta_{12}) = \frac{1}{\cos\alpha} + \frac{1}{\sin\alpha} - \frac{1/Z}{(1-\sin 2\alpha\cos\vartheta_{12})^{1/2}}\,.$$

As an aside here, let us remark that Eq. (4b), insofar as it is a two-electron $L=0$ Schrödinger equation, applies equally to bound states and to the continuum, the only difference between them being in the sign of the energy. We should actually expect an intimate connection between the ionization problem and the doubly excited states of the same two-electron atom that lie on the other side of threshold.[13] Actually, Eq. (4b) has been considered by Macek[14] in the context of doubly excited states of He.

Expanding all terms in Eq. (4b) about the Wannier direction and retaining terms up to the first nontrivial order in $\beta = \frac{1}{4}\pi - \alpha$ and $\gamma = \pi - \vartheta_{12}$, we have

$$\left(\frac{\partial^2}{\partial R^2} + k^2 + \frac{\frac{1}{4}}{R^2} + \frac{1}{R^2} \times \left\{\frac{\partial^2}{\partial\beta^2} + 4(1+4\beta^2)\left[\frac{\partial^2}{\partial\gamma^2} + \left(\frac{1}{\gamma} - \frac{1}{3}\gamma\right)\frac{\partial}{\partial\gamma}\right] - \left(-2\xi ZR - 4\eta ZR\beta^2 + \frac{R\gamma^2}{4\sqrt{2}}\right)\right\}\right)\phi(R,\beta,\gamma) = 0\,, \tag{5}$$

with

$$\xi = 2\sqrt{2} - (\sqrt{2}Z)^{-1}\,,\quad \eta = (3/\sqrt{2}) - (4\sqrt{2}Z)^{-1}\,. \tag{6}$$

The three terms in the last large parentheses represent the potential multiplied by R^2. This potential consists of (a) a Coulomb term in R with effective charge $2\xi Z$, (b) a harmonic oscillator term γ^2/R, and (c) an "antiharmonic oscillator" potential β^2/R. This and the nonappearance of linear terms in β and γ are expected because the Wannier point is a saddle point of the potential $B(\alpha,\vartheta_{12})$. Notice also in Fig. 1 the deep attractive wells at $\alpha=0$ and[15] $\frac{1}{2}\pi$ which explain the earlier remarks about the instability of wave-function propagation along $\alpha=\frac{1}{4}\pi$.

By inspection of Eq. (5), the form of a solution, at least near zero energy, suggests itself. Recall from the form of the zero-energy Coulomb functions discussed in Sec. II that in the ordinary Coulomb problem, the potential $2Z/R$ is canceled by factoring $\exp[i(8ZR)^{1/2}]$ out of the wave function. This operation leaves a residual potential proportional to $R^{-3/2}$ which converges faster than $1/R$. The analog in our problem,

$$\exp\left[i(8\xi ZR)^{1/2}\left(1 + \frac{2\eta\beta^2}{\xi} - \frac{\gamma^2}{8\sqrt{2\xi Z}}\right)\right]\,,$$

would similarly cancel the potential terms of Eq. (5) were it not for the effect of the derivatives in β and γ. To allow for these derivatives, we should expect to factor out a more general form, $\exp[icR^{1/2}\times(1+\frac{1}{2}a\beta^2+ib\gamma^2)]$, where a, b, and c are constants that can be adjusted to cancel all $1/R$ terms in Eq. (5). There is also another reason for expecting this form, this time by looking at the equation as an equation in β and γ. The ground-state wave function of a harmonic oscillator potential $R\gamma^2/4\sqrt{2}$ has the form $\exp(-bcR^{1/2}\gamma^2)$. A similar situation occurs for the β behavior, where we expect an oscillatory function, instead of a Gaussian.

Hence we write

$$\phi(R,\beta,\gamma) = \exp(icR^{1/2} + \tfrac{1}{2}iac\beta^2R^{1/2} - bcR^{1/2}\gamma^2)\,\chi(R)\,. \tag{7}$$

This form, which has been written down in analogy with the single-particle zero-energy Coulomb wave functions, is really not restricted to zero energy. Its validity depends on the relative importance of the two terms, k^2 and the Coulomb potential, in the Schrödinger equation. We can use this comparison to define two zones in which one or the other of these energies is dominant. In the "Coulomb zone," $k^2 \ll 2\xi ZR^{-1}$, the potential is dominant and the wave function will be of a zero-energy type with the form Eq. (7). Exactly at zero energy, the Coulomb zone stretches all the way to $R=\infty$. At any finite energy, however, there will always be a "far zone" in which the potential is negligible compared to k^2 and the solution (7) will not be valid. In keeping with the spirit of the threshold problem we will not look for solutions in the reaction zone which extends to finite R, but study only solutions for larger R. Further, of the two large-R regions one would expect the Coulomb zone to be dominant near threshold and we will argue, as did Wannier, that the threshold law is a feature of the wave functions in this zone.

In this section then we will study the solutions of the form Eq. (7). In Sec. VI we will look for more general solutions which are valid both in the Coulomb and in the far zone.

Let us also remark on the spin state to which the wave functions (7) belong. Interchange of $\vec{r}_1$ and $\vec{r}_2$ corresponds to $\gamma \to \gamma$, $\beta \to -\beta$. Hence Eq. (5), which depends on β^2, represents a singlet wave function. We will, therefore, see that the Wannier theory implies that for $L=0$, singlet wave functions determine the threshold behavior. This is because all $L=0$ triplet wave functions have a node along $\alpha = \frac{1}{4}\pi$.[14] Restriction to the Wannier region automatically excludes triplet states.

We will now determine $\phi(R,\beta,\gamma)$ by substituting the form (7) in Eq. (5) and again retaining terms up to the first nontrivial order, i.e., β^2/R, γ^2/R, and $R^{-3/2}$. This yields

$$\left[\frac{\partial^2}{\partial R^2} + k^2 + \frac{\frac{1}{4}}{R^2} + \frac{2\xi Z - \frac{1}{4}c^2}{R} + \frac{4\eta Z - a^2c^2 - \frac{1}{4}ac^2}{R}\beta^2 + \frac{16b^2c^2 - \frac{1}{8}\sqrt{2} - \frac{1}{2}ibc^2}{R}\gamma^2 + \frac{ic}{R^{1/2}}\left(\frac{\partial}{\partial R} + \frac{a+16ib-\frac{1}{4}}{R}\right) + \left(\text{terms in } \frac{\beta^2,\gamma^2}{R^{3/2}}, \frac{\beta^4,\gamma^4}{R}\right)\right]\chi(R) = 0 . \quad (8)$$

We now choose a, b, and c to cancel all the $1/R$ terms. This gives

$$c = (8\xi Z)^{1/2} \text{ (as expected)},$$

$$a = \tfrac{1}{2}[-\tfrac{1}{4} \pm (\tfrac{1}{16} + 2\eta/\xi)^{1/2}] = \tfrac{1}{2}[-\tfrac{1}{4} \pm \tfrac{1}{2}\mu] , \quad (9)$$

$$b = \frac{1}{64}\left[i \pm \left(\frac{9-4Z}{4Z-1}\right)^{1/2}\right] = \frac{1}{64}[i \pm 2\rho] ,$$

where μ and ρ are the parameters introduced by Wannier (see Sec. III).

The only approximation we make now is to drop in Eq. (8) the terms of higher order involving either higher powers of R^{-1} or of β^2 or γ^2. This means we consistently take into account the potential to order $R^{-3/2}$, $\beta^2 R^{-1}$, and $\gamma^2 R^{-1}$. We expect this to be adequate for large R. The following are arguments to justify this statement. First of all, in Eq. (8) there are, among others, two terms $\beta^2 R^{-1/2}(\partial/\partial R)$ and $\gamma^2 R^{-1/2}(\partial/\partial R)$. So long as $\chi(R)$ has such a form that these derivatives do not regenerate terms of lower order than β^2/R, the above procedure is consistent. In particular, we will see that for large R, $\chi(R)$ is indeed a power of R and hence the neglected terms have higher order, $\beta^2 R^{-3/2}$. A second point is that if in Eq. (7) we had not written $\chi(R)$ but $\chi(R,\beta,\gamma)$, there would have been no approximation at that stage. In Eq. (8) then we would also have had $R^{-2}(\partial^2/\partial\beta^2)$ and $R^{-2}(\partial^2/\partial\gamma^2)$ acting on χ. Again, if the dependence of χ on R turns out to be a power of R, these are higher-order terms. The final plausibility for these steps is obtained by remarking that the potential in Eq. (5) is almost like an ordinary Coulomb potential with the main dependence contained in Z/R. Everything else constitutes a slowly varying quantity in the vicinity of the Wannier point. This is particularly clear from Fig. 1, which shows that the potential remains near $-2Z/R$ a.u. over a wide range of β and γ around the saddle point. This close resemblance to the ordinary Coulomb problem justifies the adoption of the same steps that are used to analyze the ordinary Coulomb equation.[16]

We are left then with an equation for $\chi(R)$ valid for $R \ll 2\xi Z k^{-2}$:

$$\left[\frac{d^2}{dR^2} + k^2 + \frac{\frac{1}{4}}{R^2} + \frac{ic}{R^{1/2}}\left(\frac{d}{dR} + \frac{a+16ib-\frac{1}{4}}{R}\right)\right] \times \chi(R) = 0. \quad (10)$$

If we write $P(kr) = \exp(icr^{1/2})\chi_l(r)$ in the ordinary Coulomb equation [Eq. (2)], the equation we obtain for $\chi_l(r)$ coincides with Eq. (10) with $a=b=0$, $\xi=1$, and $l=-\frac{1}{2}$. (The formal appearance of a half-integer value of l in the Schrödinger equation for an n-body problem, n odd, has been noted previously.[8]) We have, therefore, arrived at a generalization of the ordinary Coulomb equation with extra potential terms in $R^{-3/2}$. The dynamic screening in α has led to an effective $-iacR^{-3/2}$ potential. That this potential is complex is again expected because we have sought solutions in a limited region of configuration space. A complex potential is the hallmark of a procedure that treats only a part of phase space; it represents the coupling of this part to the rest of the space.

The preceding development relates to Wannier's work not only through the appearance of his coefficients μ and ρ in Eq. (9), but also through a consideration of the surfaces of constant phase in Eq. (7). These surfaces consist of two alternative sets of paraboloids in $\ln R$ (or, equivalently, R) against β and γ, one for each sign in the expression for a in Eq. (9). Cross sections of these paraboloids in the (R,β) plane are shown in Fig. 2. The orthogonal trajectories of these paraboloids coincide with the Wannier orbits. In the γ direction, all orbits are converging though they also oscillate according to the cosine factor in Wannier's equa-

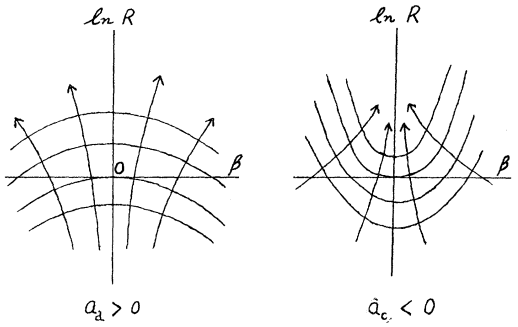

FIG. 2. Sketch of surfaces of constant phase in (R, α) plane with corresponding classical trajectories. a_c and a_d refer to converging and diverging orbits, respectively.

tion. Note that we have to choose the positive sign for Re(b) in Eq. (9) to ensure that the wave function (7) remains finite as $R^{1/2}\gamma^2$ increases. Let us also remark here that for $Z > 2$, b becomes purely imaginary. Inspection of Eq. (9) however shows that both roots lead to converging orbits (in contrast with the behavior in α) because in either case Im(b) is positive; hence the gradient of the phase converges in either case towards $\gamma = 0$ as R increases. Note that the negative root leads to $b = 0$ at $Z = \infty$ (where the angular correlation might be expected to disappear). The Appendix discusses the solutions of Eq. (10) for zero energy and their extension to finite energy. However, we only wish to illustrate how the converging and diverging solutions are to be superposed in the Coulomb zone and point out the implications of this superposition for the threshold law. For this purpose, it is sufficient to look at the solutions for zero energy and large R; they are

$$\chi(R) \sim R^{1/4-a-\bar{b}} \quad , \tag{11}$$

with $\bar{b} = 16ib$.

Hence, the full solutions $\phi(R, \beta, \gamma)$ in Eq. (7) have $\chi(R)$ just as a power of R. Further, with $a = b = 0$, the result is in agreement with the ordinary zero-energy Coulomb functions because $R^{1/2}J_0[(8ZR)^{1/2}]$ goes like $R^{1/4}$ for large R. The relation of the phase of ϕ to Wannier's orbits has already been discussed. The alternative values of a yield two independent solutions in Eq. (11) and the general form of the wave function is some linear combination of them,

$$\phi(R, \beta, \gamma) = Ae_c R^{1/4-a_c-\bar{b}} + Be_d R^{1/4-a_d-\bar{b}} \quad . \tag{12}$$

Here a_c and a_d are the values of a in Eq. (9) with the negative and positive signs, respectively, and

$$e_{c,d} = \exp[(icR^{1/2})(1 + \tfrac{1}{2}\beta^2 a_{c,d} + i\gamma^2 b)] \quad .$$

A and B are constants which, it is envisaged, will be determined by the solutions of the Schrödinger equation in the reaction zone. The understanding is that these small-R solutions are expanded at the boundary of the reaction zone into a basis set that is valid for the Coulomb zone. We have sought here solutions in the Coulomb zone which will constitute the elements of such a basis set that dominate for large R because the threshold law is a feature of these solutions, which represent the coupling of the reaction-zone solutions to infinity. For the purpose of establishing the threshold law, we only need to note that A and B are determined by the small-R solutions and that B/A is k independent.

V. THRESHOLD LAW FOR ELECTRON-ATOM IONIZATION

We now have wave functions that are accurate to $O(R^{-1})$ in the Coulomb zone which extends for zero energy all the way to $R = \infty$. What we wish to consider in this section is a procedure to establish the Wannier threshold law starting from these wave functions. General solutions of the two-electron Schrödinger equation at arbitrary energy will also have two terms in the Coulomb zone, one corresponding to converging and the other to diverging orbits. Wannier's work suggests that we determine the amplitude of the divergent solution present in the full solution; more precisely, we only require the k dependence of this amplitude.

This determination will be carried out by adapting a method[17] for establishing the threshold dependence of the phase shift for scattering by a short-range potential. The zero-energy solution outside the range of the potential has the form $Ar^l + Br^{-(l+1)}$ analogous to Eq. (12). This solution can be represented as a superposition of solutions of the free-particle wave equation at nonzero energy and normalized per unit volume, through multiplication by a normalization factor $f(k) = k^l$ and algebraic manipulation:

$$f(k)[Ar^l + Br^{-(l+1)}] = A(kr)^l + k^{2l+1}B(kr)^{-(l+1)} \tag{13}$$

The factors $(kr)^l$ and $(kr)^{-(l+1)}$ necessarily represent the leading terms of the $kr \to 0$ expansion of the regular and irregular solutions (normalized per unit volume) of

$$\left(\frac{d^2}{dr^2} + k^2 + \frac{l(l+1)}{r^2}\right) u(r) = 0 \quad ,$$

which is the relevant equation for this problem at r values outside the range of the potential. This statement does not depend on explicit knowledge of the full solutions $j_l(kr)$ and $n_l(kr)$. Once we know the zero-energy form and observe from the structure of the equation that r occurs in the combination kr, we can infer the small argument expansion of the solutions for arbitrary energy and further conclude that the leading term of $\tan\delta$, where δ is the phase shift, has the k dependence k^{2l+1} given in Eq. (13).

In our problem we know that the converging and diverging waves, multiplied by A and B as in Eq. (12), must represent the zero-energy Coulomb-zone forms of unknown functions of R, β, and γ. We concentrate here on the dependence on R because the dependence of the potential on β and γ in the Wannier region has already been taken into account. Since the dependence of the potential on R in this region is of the form Z/R, it is clear that the unknown functions are functions of kR and Z/k. We expect then that the general solutions have the structure

$$F(k)[Au_c(kR, Z/k, \beta, \gamma) + BC(k)u_d(kR, Z/k, \beta, \gamma)] . \tag{14}$$

In the Coulomb zone, this must match Eq. (12) and hence must take the following form so that the R dependence agrees with Eq. (12):

$$F(k)[Ae_c(kR)^{1/4-a_c-\bar{b}} + BC(k)e_d(kR)^{1/4-a_d-\bar{b}}] . \tag{15}$$

When $k \to 0$ this should continue smoothly into Eq. (12), which means that a common k dependence should factor out of the expression inside the brackets. For this we must have

$$C(k) = k^{a_d-a_c} = k^{\mu/2} . \tag{16}$$

Further, if we want these two-electron wave functions (14) to be normalized per unit volume, we can get the form of $F(k)$ because Eq. (15) must reduce to the ordinary Coulomb solution when $a = \bar{b} = 0$. We saw in Sec. II that volume-normalized Coulomb solutions are, in the Coulomb zone, $k^{1/2}R^{1/4}\exp[i(8ZR)^{1/2}]$. Hence $F(k) \propto k^{1/4}$.

With these choices for $F(k)$ and $C(k)$, Eq. (14) does represent the structure of general two-electron wave functions with the right limiting property that in the Coulomb zone they match the zero-energy form [Eq. (12)] as $k \to 0$. In the asymptotic limit on the other hand, $k^2R \gg 2\xi Z$, the expression (14) should reduce to the asymptotic solution given by Peterkop,[18] which in the Wannier direction has the form

$$\phi(R, \beta, \gamma) \sim \exp[ikR + (iZ/k)(\xi + 2\eta\beta^2 - \gamma^2/8\sqrt{2}Z)\ln 2kR] . \tag{17}$$

We will actually demonstrate in Sec. VI that this is so, but for the present we only need the result that the k dependence of the diverging part is $k^{\mu/2+1/4}$. Notice particularly that this expression does not involve b but only the parameters a, in agreement with Wannier's conclusion that only the behavior in α, not the one in ϑ_{12}, is crucial to the threshold law.

Wannier argued from statistical considerations that the converging orbits form a set of measure zero compared to the diverging ones and hence are not important for the threshold law. This would imply that though in Eq. (12) or Eq. (14), A and B are determined by the small-R solutions, for the orbits relevant to *double escape*, A is very small (of measure zero) compared to B. Wannier's argument may imply that A vanishes for ionization, in the "initial feeding" into the Coulomb zone from the small-R solutions at the boundary of the reaction zone. This question remains as a topic for further research. For the present, if we adopt Wannier's argument that it is the diverging orbits that are important for the threshold law, we have the correct k dependence of the final state of the wave function to go into Eq. (3). Combining $C(k)$, $F(k)$, and $k^{-5/2}$, which stands for volume normalization as discussed in Sec. II ($N = 6$), one has $k^{\mu/2+1/4-5/2}$ as the k dependence of the wave function to go into the matrix element in Eq. (3); therefore,

$$\sigma \propto E^{\mu/2-1/4} , \tag{18}$$

which is Wannier's result.[19] We again emphasize that the preceding paragraphs in this section have indicated *a possible way* of understanding the Wannier threshold law starting from the wave functions derived earlier. It is still possible that the "true" threshold law is different, arising from other quantum-mechanical effects which make regions of configuration space other than the Wannier region ($\alpha = \frac{1}{4}\pi, \vartheta_{12} = \pi$) important for double escape. Further, it may be possible to use the wave functions derived here in a different way from the one we have given to arrive at Eq. (18). What is certain is that the quantum-mechanical equation does have solutions in the Wannier region which correspond to his classical orbits.

For $Z = 1$, Eq. (18) gives $\sigma \propto E^{1.27}$. This is not inconsistent with experimental observations,[20] which do show a nonlinear behavior of the cross section at threshold.

Let us now consider the implications of the finite-energy solutions [Eqs. (15) and (17)] for the correlation in energy and angle. In our picture, the two electrons start from the reaction zone correlated both in energy and angle; the correlation is expressed by the form of Eq. (15) and the fact that Eq. (15) holds only near the Wannier direction. In the Coulomb zone, the angular correlation remains, even increasing slightly, but there are two kinds of behavior in α—the converging orbits lead to a greater energy correlation and the diverging orbits to less. However, since it is necessary that the wave function still be confined to around the Wannier direction until it emerges into the far zone, there is still energy correlation for all the orbits. Once in the far zone, the electrons are essentially free and double escape cannot be pre-

vented. However, in this zone, the energy correlation is gradually lost. We will see this explicitly when we derive far-zone solutions in Sec. VI, but this result is anticipated by the asymptotic form [Eq. (17)]. Analyzed in terms of orbits, the gradient of the phase of this expression converges to $\gamma = 0$, but diverges from $\beta = 0$ as R increases. The implication for experimental observation is that for observations near threshold, there is strong angular correlation but, with regard to energy, any partitition of energy between the two electrons is equally likely, a result borne out by computer calculations.[21] The significant point is that equipartition of energy is as likely as any other partition near threshold, whereas above threshold, it is highly unlikely; one electron normally carries away most of the available energy.[2] Again, it is interesting that in the experiments of Ehrhardt[12] on e + He ionization, which show angular correlation near threshold, when the incident energy is 30 eV or lower, he readily picks up the two outgoing electrons with equal energy.

VI. WAVE FUNCTIONS AT FINITE ENERGY

The central argument in Sec. V was that threshold laws could be derived once the zero-energy wave functions are known. Thus in Sec. IV we focused on obtaining a limited solution of the Schrödinger equation which would be valid only in the Coulomb zone. We will now sketch a derivation of solutions to Eq. (5) that are more general, stretching out into the far zone and all the way to $R = \infty$ for nonzero (though small) energy. This will also illustrate what was involved in the arguments in Sec. V that went from Eqs. (12) to (16).

Close to zero energy, for large R, but in a region dominated by the Coulomb potential ($k^2R \ll 2\xi Z$), we showed that the solution has the form (7). The $R^{1/2}$ in the exponent was introduced as characteristic of the Coulomb zone. To get more general solutions but still focusing on the Wannier direction, we have only to relax the assumption (7) for the dependence on R. The dependence on β and γ is, of course, unaffected because it is characteristic of the Wannier direction.

Therefore let us put

$$\phi(R,\beta,\gamma) = \exp(if + ig\beta^2 + ih\gamma^2)\chi(R)\,, \qquad (7')$$

where f, g, and h are functions of R.

As before, we will substitute this form in Eq. (5) and retain terms up to the first nontrivial order in the potential.

Substituting Eq. (7') in Eq. (5), we have

$$\left[\frac{d^2}{dR^2} + 2if'\frac{d}{dR} + \frac{\frac{1}{4}}{R^2} + \left(k^2 + \frac{2\xi Z}{R} - f'^2\right) + if'' + \frac{2ig + 16ih}{R^2} + \left(\frac{4\eta Z}{R} + ig'' - 2f'g' - \frac{4g^2}{R^2} + \frac{64ih}{R^2}\right)\beta^2 + \left(-\frac{1}{4\sqrt{2R}} + ih'' - 2f'h' - \frac{16h^2}{R^2} - \frac{8ih}{3R^2}\right)\gamma^2\right]\chi(R) = 0\,, \qquad (8')$$

where primes denote differentiation with respect to R.

First of all choose f so that

$$k^2 + 2\xi Z/R - f'^2 = 0.$$

If $k^2R \ll 2\xi Z$, this equation leads back to the old result $f = (8\xi ZR)^{1/2}$, as it should. In the opposite limit $k^2R \gg 2\xi Z$, it gives $f = kR + (\xi Z/k)\ln 2kR$, in agreement with Eq. (17).

To determine g and h, we know that in one limit, $k^2R \ll 2\xi Z$, g and $h \propto R^{1/2}$. In the opposite limit we know from Eq. (17) that g and $h \propto \ln R$. In either case, in both the last two large parentheses in Eq. (8'), the second and fifth terms are of higher order than the others in powers of R^{-1}. Therefore we can consistently drop these terms [they are the terms we had dropped in Eq. (8) also] and set the remaining sums equal to zero, so that we eliminate coefficients of β^2 and γ^2 in Eq. (8'). This gives

$$4\eta ZR^{-1} - 2f'g' - 4g^2R^{-2} = 0\,,$$

$$(4\sqrt{2R})^{-1} + 2f'h' + 16h^2R^{-2} = 0\,. \qquad (9')$$

It is easily verified that with $f = cR^{1/2}$, $g = \frac{1}{2}acR^{1/2}$, and $h = ibcR^{1/2}$, Eq. (9') reduces to Eq. (9), giving the values of a, b, and c that we obtained earlier in the Coulomb zone. The presence of g^2 and h^2 suggests that Eq. (9') can be cast in Riccati form. For this purpose, one needs to pass over from g and h to new functions $\tilde{g}$ and $\tilde{h}$, such that in the nonlinear equations for $\tilde{g}$ and $\tilde{h}$ the coefficient of the quadratic terms $\tilde{g}^2$ and $\tilde{h}^2$ is unity:

$$g = \tfrac{1}{2}R^2(k^2 + 2\xi Z/R)^{1/2}\tilde{g}\,.$$

This then casts the equations for $\tilde{g}$ and $\tilde{h}$ into Riccati form from which a standard transformation gives linear, but second-order differential equations for $\exp(\int\tilde{g}\,dR)$ and $\exp(\int\tilde{h}\,dR)$. These steps can be condensed into the statement that from g and h we can pass over to new functions u and v which obey the hypergeometric differential equation. We have

$$g=\tfrac{1}{2}R^2\left(k^2+\frac{2\xi Z}{R}\right)^{1/2}\frac{d}{dR}\ln(R^{2a}u)\ ,$$

$$h=\tfrac{1}{8}R^2\left(k^2+\frac{2\xi Z}{R}\right)^{1/2}\frac{d}{dR}\ln(R^{\bar{b}}v)\ ,$$

where

$$u={}_2F_1(2a,\ 2a+1,\ 4a+\tfrac{3}{2},\ -k^2R/2\xi Z)\ ,$$
$$v={}_2F_1(\bar{b},\ \bar{b}+1,\ 2\bar{b}+\tfrac{3}{2},\ -k^2R/2\xi Z)\ , \qquad (9'')$$

with a and $\bar{b}$ defined by Eqs. (9) and (11), $\bar{b}=16ib$.

Notice that the ${}_2F_1$ in Eq. (9'') are related to the Legendre functions $P^{\alpha}_{1/2}[(1+k^2R/2\xi Z)^{1/2}]$; hence these equations correspond to the more general orbits given by Wannier in an appendix. Of course, in the two limits $k^2R\ll 2\xi Z$ and $k^2R\gg 2\xi Z$, the limits of u and v are such that Eq. (7') reduces to the solutions for the Coulomb zone and the asymptotic form, i.e., to Eq. (7) and Eq. (17), respectively.

Equation (8') now reads

$$\left(\frac{d^2}{dR^2}+2if'\frac{d}{dR}+\frac{\frac{1}{4}}{R^2}+if''+\frac{2ig+16ih}{R^2}\right)\chi(R)=0\ . \qquad (10')$$

This is the generalization of Eq. (10). Substitution of f and g shows that the dynamic screening gives a $R^{-3/2}$ potential in the Coulomb zone but a $R^{-2}\ln R$ potential[22] asymptotically [see Eq. (17)]. We will not consider the general solutions of Eq. (10') here, but for large R a Glauber-type approximation that drops the first and third terms[23] leads to the solution[24]

$$\chi(R)=R^{-a-\bar{b}}v^{-1}u^{-1/2}[R/(k^2R+2\xi Z)]^{1/4}\ . \qquad (11')$$

For $k^2R\ll 2\xi Z$, this reduces to Eq. (11). For $k^2R\gg 2\xi Z$, the asymptotic form[25] of ${}_2F_1$ gives $u\sim(k^2R/2\xi Z)^{-2a}$. Hence Eq. (11') becomes in this limit $\chi(R)\sim k^{2(-1/4+a+\bar{b})}$, which is independent of R, as one would expect from Eq. (17).

We thus have general solutions agreeing with our earlier knowledge of the Coulomb zone and the asymptotic solution (17). The steps from Eq. (12) to (16) can now be understood as follows. Since Eq. (11') reduces to Eq. (11) in the Coulomb zone, in this zone we have to take a superposition of the two solutions with alternative values of a such that their relative ratio B/A is independent of energy, just as we did in Eq. (12). This automatically leads to an energy dependence k^{μ} for the relative ratio of the diverging and converging parts at $R=\infty$. Once again, because R should appear in the combination (kR), we have to cast this superposition in the form of Eq. (15); the relative ratio then has the k dependence given by $C(k)$ in Eq. (16) over the entire range of Coulomb and far zones.

Note that in Eqs. (7'), (9'), and (11'), we have obtained a wave function which continuously evolves from the form in the Coulomb zone (corresponding equations in Sec. IV) to the final asymptotic form. Here then we have a solution which carries complete information on the energy and angular correlation at each state of the escape process and gives a quantitative realization of the remarks at the end of Sec. V on what happens to these correlations during the escape.

VII. CONCLUDING REMARKS

We conclude with a few remarks on the range of validity of the threshold law and the connection of the continuum wave functions that we have derived to Macek's results on doubly excited states.

The picture of dynamic screening and of its influence on the escape process makes clear that the Wannier threshold law will be correct only so long as no other interaction can give an appreciable contribution to the energy or the energy exchange between the electrons once they are in the far zone, i.e., once past $R\simeq 2\xi Zk^{-2}$. Thus if other long-range forces are present in the system, their contribution to the energy at this radius must be negligible compared to k^2. For example, in the ionization of an atom with more than one electron, the polarizability of the core will play a major role in determining the range of validity—the stronger the polarizability, the shorter the energy range over which the Wannier law should be expected to be valid.

Let us now compare our work to that on doubly excited states of atoms. Apart from its conceptual interest, this comparison is suggestive because it hints at a way of deriving a complete basis set for the two-electron Schrödinger equation in the Coulomb zone. Recall that so far we have focused on energies near threshold and hence on the Wannier direction. The wave functions that we have derived are the ones relevant for the threshold law, but they constitute only the first members of a full basis set which is valid for arbitrary α and ϑ_{12}. What is this set that would serve as a complete basis for expansion of the small-R solutions? The answer to this may come by relating our work to Macek's, where the same two-electron equation (4b) was considered but in the context of doubly excited states of He**. The restriction to the Wannier region in α and ϑ_{12} was not made but some other simplifying assumptions were made in order to solve the equation. A simultaneous generalization of this paper and Macek's may indicate how the various assumptions in the two papers could be relaxed.

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APPENDIX

In Sec. II, we saw that the threshold law follows from leading terms of the low-energy wave functions when expanded in k^2, which is to say, from the zero-energy wave functions alone. However, it is of interest, particularly in order to see the role of $k^2R \simeq 2\xi Z$, to get more general solutions in the region $k^2R \ll 2\xi Z$ as a series in $k^2R/2\xi Z$. To investigate solutions of (10) for small k, let us first write it in a form suitable for passage to single-electron Coulomb functions:

$$\left(\frac{d^2}{dR^2} + k^2 + \frac{\frac{1}{4} - (l+\frac{1}{2})^2}{R^2} + \frac{ic}{R^{1/2}}\frac{d}{dR} + \frac{ic}{R^{3/2}}(a - \tfrac{1}{4} + 16ib)\right)\chi(R) = 0 \quad . \tag{A1}$$

Equation (10) is identical to (A1) with $l = -\frac{1}{2}$. On putting $a = b = 0$ and $c = (8Z)^{1/2}$ in (A1), we have the ordinary two-body Coulomb wave function.

With $s = R^{1/2}$ and $\chi(R) = e^{-ics}s^{-2l}F(s)$, we have

$$\left(\frac{d^2}{ds^2} + 4k^2s^2 + 8\xi Z - \frac{4l+1}{s}\frac{d}{ds} + \frac{4ic(a+16ib)}{s}\right) \times F(s) = 0 \quad . \tag{A2}$$

We solve this as an expansion for small k by taking the Laplace transform

$$Y(p) = \int_0^\infty e^{-ps}F(s)\,ds \quad , \tag{A3}$$

$$(p^2 + 8\xi Z)\frac{dY}{dp} + [(4l+3)p - 4ic(a+16i\bar{b})]Y = -4k^2\frac{d^3Y}{dp^3} \quad . \tag{A4}$$

The zeroth-order solution (or alternatively the zero-energy solution) is obtained by dropping the right-hand part in (A4). The solution for $Y(p)$ then is straightforward and the inverse transform gives

$$F(s) = e^{-ics}s^{4l+2}\,{}_1F_1(2l + \tfrac{3}{2} - 2(a+\bar{b}),\ 4l+3,\ 2i(8\xi Z)^{1/2}s). \tag{A5}$$

For very large R, this leads to $\chi(R)$ as a power of R, as in Eq. (11). Also notice that for $a = b = 0$ the ${}_1F_1$ reduces to a Bessel function $J_{2l+1}((8\xi ZR)^{1/2})$, which we know from Sec. II to be a factor in the zero-energy wave function of the ordinary Coulomb equation.

Successive terms in the series for $Y(p)$ or $F(s)$ can now be generated recursively from Eq. (A4). The a and b make only for algebraic complexity and since the features we want to demonstrate can be seen from the ordinary Coulomb case, we will now set $a = b = 0$ and $\xi = 1$ in (A4).

We have as solutions

$$Y(p) = (p^2 + 8Z)^{-(2l+3/2)}\left[1 + 8k^2(2l+\tfrac{5}{2})\left(-\frac{(2l+\frac{3}{2})(2l+2)}{(p^2+8Z)^2} + \frac{16Z(2l+\frac{3}{2})(2l+\frac{7}{2})}{(p^2+8Z)^3}\right) + O(k^4)\right] , \tag{A6}$$

and, therefore,

$$F(s) = \frac{\pi^{1/2}}{\Gamma(2l+\frac{3}{2})}\left(\frac{R}{32Z}\right)^{l+1/2}\left[J_{2l+1}((8ZR)^{1/2}) - \frac{k^2R}{2Z}(l+1)J_{2l+3}((8ZR)^{1/2}) + \frac{2iZ}{3k}\left(\frac{k^2R}{-2Z}\right)^{3/2}J_{2l+4}((8ZR)^{1/2}) + \cdots\right]. \tag{A7}$$

We remark that when a and b are retained in (A4) we get a similar series with each Bessel function replaced by the corresponding confluent hypergeometric equation as in (A5). Further note that when $a = b = 0$, (A4) is really a function of p^2, not of p. Therefore, when $a \neq 0$ and $b \neq 0$, we get additional terms in the series for $F(s)$ which involve factors in $\ln R$, which is a hallmark of the three-body solutions. Instead of giving the complicated series for $F(s)$, we give below the more compact form for $Y(p)$ for this problem. Writing

$$Y(p) = \sum_{n=0}^{\infty} Y_n(p)$$

as a series for $Y(p)$ in powers of k^2, we get

$$Y_n(p) = 4k^2Y_0(p)\int_p^\infty (p^2 + 8\xi Z)^{-1}Y_0^{-1}(p)\frac{d^3}{dp^3}Y_{n-1}(p)\,dp \, ,$$

with

$$Y_0(p) = (p^2 + 8\xi Z)^{-2l-3/2}[p - i(8\xi Z)^{1/2}]^{2(a+\bar{b})}$$

$$\times[p+i(8\xi Z)^{1/2}]^{-2(a+\bar{b})}.$$

This gives a recursive series for the Laplace transform of $F(s)$ for the two-electron problem. Since this series is a function of k^2, it may be useful also for application to doubly excited states of atoms.

Returning to the single-electron case, one can see that (A7) is the $k^2R \ll 2Z$ limit of the Coulomb continuum wave function as follows. Equation (4.7) of Ref. 26 with $2k\xi = t$ gives the integral form of the Coulomb wave function:

$$\phi(R) = R^{-(l+1)} \int e^{-iRt} \left(\frac{t-k}{t+k} \right)^{iZ/k} \frac{dt}{(t^2-k^2)^{l+1}} \,. \tag{A8}$$

The contour has to enclose the branch points at $t = \pm k$. If, as we will see below, there is a regime in which the main contribution is from t very large compared to k, then we can expand all terms in powers of k/t. This gives

$$\phi \propto R^{-(l+1)} \int \frac{e^{-iRt} \exp[(-2iZ/k)(k/t + k^3/3t^3 + \cdots)]}{t^{2l+2}(1-k^2/t^2)^{l+1}} dt.$$

Putting $x = -i(R/2Z)^{1/2} t$ gives

$$\phi \propto R^{-1/2} \int \frac{\exp[(2ZR)^{1/2}(x - 1/x)]}{x^{2l+2}} \times \left\{ 1 + k^2 \left[\frac{-R}{2Zx^2} + \frac{2Z}{3} \left(\frac{R}{2Z} \right)^{3/2} \frac{1}{x^3} \right] + \cdots \right\} dx. \tag{A9}$$

The branch points are now at $x = \pm ik(R/2Z)^{1/2}$. Notice, however, that there are two saddle points at $x = \pm i$. Thus when the main contribution is from the vicinity of the saddle point, i.e., when $k^2R \ll 2Z$, the small argument expansion of (A8) to yield (A9) is justified. Recognizing the integral form of the Bessel function, we see that (A9) gives the series (A7). However, as k increases, the branch points move away from near the origin along the imaginary axis in the x plane and finally around $k^2R \simeq 2Z$ they move past the saddle points. We then have to go back to the original form (A8) or the usual Coulomb wave function

$$R^{l+1} e^{-ikR} {}_1F_1(l+1-iZ/k,\ 2l+2,\ 2ikR) \,.$$

This analysis[27] of the ordinary Coulomb equation shows clearly the role of $k^2R = 2Z$. Because of the close similarity of the two-electron wave equation (A1) to the above Coulomb problem, it may also perhaps be exploited to get some insight on the general two-electron wave functions.

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[1]G. H. Wannier, Phys. Rev. 90, 817 (1953).

[2]U. Fano, Comments At. Mol. Phys. 1, 159 (1970).

[3]R. Peterkop and A. Liepinsh, in *Proceedings of the Sixth International Conference on the Physics of Electronic and Atomic Collisions* (MIT Press, Cambridge, Mass., 1969), p. 212.

[4]E. P. Wigner, Phys. Rev. 73, 1002 (1948).

[5]This is because Ψ_i^+ differs from ψ_i by terms involving the potential. Since the threshold law is a feature of the form of the potential and not its strength, it should remain unchanged if we change the strength of the potential, in particular, if we make the strength very small. Hence, terms in the transition matrix element in Eq. (1) beyond the Born term, being of higher order in the strength, are not material to the threshold law.

[6]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun, Natl. Bur. Std. (U.S.), Appl. Math. Series–55 (U.S. GPO, Washington, D.C., 1964), Chap. 14.

[7]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, 2nd ed. (Addison-Wesley, Reading, Mass., 1965), Sec. 36.

[8]L. M. Delves, Nucl. Phys. 9, 391 (1958–1959). There is some question about the correctness of the E^2 result; in particular, arguments about analyticity of the scattering amplitude indicate that there should be factors in $\ln E$ in the threshold behavior. See A. J. Dragt and R. Karplus, Nuovo Cimento 26, 168 (1962).

[9]M. R. H. Rudge and M. J. Seaton, Proc. Roy. Soc. (London) A283, 262 (1965); S. Geltman, *Topics in Atomic Collision Theory* (Academic, New York, 1969), Sec. 19; A. Temkin, Phys. Rev. Letters 16, 835 (1966).

[10]R. Peterkop, in Ref. 3, p. 936.

[11]At threshold, this would seem to be the relevant value of L. Further, there is an indication that the restriction to $L = 0$ is not crucial for the threshold law. See R. Peterkop and P. Tsukerman, in Ref. 3, p. 209; Zh. Eksperim. i Teor. Fiz. 58, 699 (1970) [Sov. Phys. JETP 31, 374 (1970)]. See also Ref. 23 of the present paper.

[12]H. Ehrhardt, K. H. Hesselbacher, and K. Willmann, Ref. 3, p. 217.

[13]In fact this connection can be exploited to derive a threshold law by approaching the ionization threshold from below. See A. Temkin, A. K. Bhatia, and E. Sullivan, Phys. Rev. 176, 80 (1968). The procedure seems to have, however, numerical difficulties and the results are still inconclusive.

[14]J. Macek, J. Phys. B 1, 831 (1968).

[15]Because the electrons are identical particles, it is sufficient to look at the potential in one quadrant alone, $0 \leq \alpha \leq \frac{1}{4}\pi$, $0 \leq \vartheta_{12} \leq \pi$, as in Fig. 1.

[16]Our procedure can also be interpreted as a partial separability, to order $R^{-3/2}$, of Eq. (5) in terms of the variables R, $R^{1/4}\beta$, and $R^{1/4}\gamma$.

[17]I thank Professor L. Spruch for the argument on the elastic scattering threshold law which was given in a seminar at the Boulder Summer School, 1968 (unpublished). The analogy between our problem and this argument lies in the fact that in both cases we have two terms which we know at zero energy and from this we determine the k dependence of one part which is of interest. The analogy is, however, limited to this aspect because the way the two terms arise and the reason for our interest in one of them are quite different in the two problems.

[18]R. Peterkop, Latvijas PSR Zinatnu Akad. Vestis 9, 79 (1960); also R. Peterkop and A. Liepinsh, Ref. 3, Eq. (12). See also the discussion after Eq. (11′) in Sec. VI.

[19]That the classical derivation gives the correct threshold law even though, at first sight, one expects WKB and classical analyses to break down near threshold is because of the long-range nature of the Coulomb potential. In the Coulomb zone, the potential leads to characteristic $\exp[i(8ZR)^{1/2}]$ oscillations, i.e., relatively rapid oscillations. Outside this region, the wavelength of the oscillations becomes k^{-1}. Thus when $k \to 0$ even though the latter wavelength becomes large, the important point is that the Coulomb zone expands, stretching to $R = \infty$ at threshold. This statement is expressed mathematically by saying that

$$\frac{d\lambda}{dR} = \frac{d}{dR}\left(k^2 + \frac{2\xi Z}{R}\right)^{-1/2}$$

is much larger than unity for all values of large R. The argument that, paradoxically, a WKB treatment becomes better near threshold should be expected to be valid for any long-range force (at least for $l = 0$ states. For non-s states, there will be a repulsive angular momentum potential far out which may limit the argument to potentials with r^{-n}, $n < 2$) and may be of interest particularly for systems in which polarizability dominates the threshold behavior.

[20]J. W. McGowan, Science 167, 1083 (1970), and references therein.

[21]I. Vinkalns and M. Gailitis, in *Proceedings of the Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad*, 1967 (Leningrad Nauka, Leningrad, 1967), p. 648.

[22]This imaginary potential adds to the angular momentum giving an effective complex angular momentum, somewhat like the Damburg-Gailitis effect for $e+H$ scattering below an excitation threshold. This suggests that this potential may be a manifestation of the doubly excited states with large dimensions.

[23]Neglect of the R^{-2} term relates to the earlier remark (Ref. 11) that the restriction to $L = 0$ is not crucial for the threshold law. In our derivation, the threshold law follows from the behavior in the Coulomb zone where the $1/R$ and $R^{-3/2}$ potentials dominate any R^{-2} potential due to non-S states.

[24]It is instructive to examine Eq. (11′) for the light it throws on Coulomb functions normalized per unit energy. This equation with $a = b = 0$ gives in the Coulomb zone $\chi(R) = R^{1/4}$, whereas in the asymptotic limit it gives $k^{-1/2}$. This expresses the fact that energy-normalized functions $R^{-1/2}J_{2l+1}(8ZR)^{1/2})$, which are independent of energy in the Coulomb zone, connect to the asymptotic form $R^{-1}k^{-1/2}\exp[ikR + (iZ/k)\ln 2kR]$, which is more easily recognized to be an energy-normalized form because spherical waves normalized per unit energy, i.e., $k^{1/2}j_l(kr)$, have exactly the same form at ∞ except for the phase.

[25]See Ref. 6, Eq. (15.3.14).

[26]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).

[27]The k^2 expansion in (A7) has been derived in many different ways. See, for instance, F. L. Yost, J. A. Wheeler, and G. Breit, Phys. Rev. 49, 174 (1936); J. G. Beckerley, *ibid.* 67, 11 (1945); and M. Abramowitz, J. Math. Phys. 33, 111 (1954). The two derivations we present are both simple and of interest in their close connection to the two-electron wave functions and for seeing the passage from the Coulomb to the far zone.

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Optical Potential for the Rotational Excitation of Diatomic Molecules by Atoms*

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By restricting attention to a single open scattering channel at a time, it is found that an optical potential, accurate to second order in the scattering potential, can be easily derived for the example of rotational excitation of a rigid rotator by a structureless atom. The resulting equations are contrasted with those derived from the close-coupling method. In cases where many open channels are present, the optical-potential method seems to offer many advantages over close coupling. Various practical methods for improving the accuracy of the optical potential beyond second order are discussed.

I. INTRODUCTION

The close-coupling method of Massey and Mohr[1] has received widespread attention ever since digital computers have made feasible the solution of many simultaneous ordinary differential equations. The