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Theory of Electronic Transitions

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Abstract

We investigate scattering of electrons from atoms in the nonrelativistic energy range. In contrast to the pioneer work by Born, we take correlation properly into account and describe electrons by waves rather than by mass points. To this end, we start from a novel parabolic partial differential equation, which resembles the inhomogeneous heat equation. Calculation of the kernels for incoming and outgoing waves allows us to formulate initial value problems. A converging Fresnel distribution is shown to control the incident electron and pulls the target electron onto an equilibrium location. The electron-electron interaction is here attractive. Finally, the two electrons are attracted by the nucleus and arrive at a triple condensation point, where they form a compound state comparable to a Cooper pair. This three-body configuration is highly unstable, described by an unstable Fresnel distribution, and leads finally to excited target states plus an escaping electron. There is no way for a one-step transition. The excitation process always goes through a ladder consisting of Fresnel states. The Wannier mode has been identified as an unstable Fresnel distribution, which is not an energy eigenstate, but it is an eigenstate of the action curvature. This unusual mode cannot be expected as a discrete line in a Rydberg spectrum, but seems to manifest itself as noise. We show that this noise is heavily suppressed near the threshold.

Keywords

Correlation, Electron Atom Scattering, Electron Pair Formation

1. Introduction

The subject of electronic excitation of atoms by electron impact deserves renewed attention because of its growing field of applications in nature.

Usually, our understanding of an excitation rests on the model of a billiard electron-electron collision where the nucleus acts only as a spectator [1].

The present article goes far beyond that model. Instead of employing unrealistic

speculations, we solve a novel transport equation in terms of a parabolic partial differential equation, which we cast into an initial value problem [2].

Our transport equation delivers the combined charge distribution of target **plus** projectile at any stage of the collision.

According to our analysis, the incoming electron does not kick a target electron, but it pulls it onto an unstable equilibrium. During this stage of the collision, two electrons (the target and the projectile electron) are involved. The electrons form a pair comparable to a Cooper pair [3]. In contrast to familiar Cooper pairs in superconductivity, our pair is stabilized by the Coulomb field of the nucleus rather than by phonons from a lattice. The wave function of our pair is a stable Fresnel distribution. Along that path, the electron pair arrives at the triple condensation point (TCP) consisting of a nucleus + two electrons.

The configuration of the TCP is, of course, unstable. Its decay starts from the TCP on top of a potential ridge and arrives in a potential valley where final target states are located.

The intermediate Fresnel state is not a directly observable state but a member of a lake filled with stable and unstable two-electron pairs. They are not energy eigenfunctions, but they are identified by the curvature of the potential ridge.

Our work offers at last three advantages:

1) Our method can easily be extended to many-electron atoms and molecules.

2) We employ calculus, including correlation, and avoid unrealistic assumptions.

3) The Wannier phenomenon appears quite naturally in a lake of Fresnel distributions.

2. Geometric Aspects

We consider here one nucleus of charge Z surrounded by N electrons. The electron-nucleus potential attraction reads

$$V = -Z\sum_{i=1}^{N}\frac{1}{r_i} \tag{1}$$

It is easily seen that this potential is unstable on any sphere Ξ_N with radius R given by

$$R = \sqrt{\sum_i r_i^2} \tag{2}$$

To see that we search for a stationary potential value with a constraint. Thus, we treat the function

$$Y = V + \lambda\left(R^2 - \sum_i r_i^2\right) \tag{3}$$

where λ is a Lagrange multiplier. Differentiation delivers.

1) All electron-nucleus separations are equal.

2) λ depends only on Z, R, and N.

3) The second derivative identifies the stationary point as a local maximum on the sphere Σ_N.

The present paper treats for the purpose of illustration only the two-electron case. A treatment of more electrons will be presented shortly.

We start now with two electrons using polar coordinates for electron-nucleus separations given by

$$r_1 = R\sin\alpha; r_2 = R\cos\alpha \tag{4}$$

The corresponding potential (1) reads then

$$V = \frac{C(\alpha)}{R} \tag{5}$$

with

$$C(\alpha) = -Z\left(\frac{1}{\sin\alpha} + \frac{1}{\cos\alpha}\right) = -Z\sqrt{2}\frac{\cos(\alpha - \alpha_0)}{\sin 2\alpha} \tag{6}$$

a_0 given by $a_0 = \pi/4$.

3. Hamilton-Jacobi Equation

We continue with classical mechanics. In contrast to Wannier [2], however, we prefer the Hamilton-Jacobi equation instead of the Lagrange equations. This choice brings us immediately close to quantum mechanics.

For the purpose of simplicity we treat here only s^2 confgurations because other angular momenta do not lead to any other excitation mechanisms. The Hamilton function reads in the case of $s^2\ {}^1S$ configurations

$$H_{\text{adiabatic}} = \frac{1}{2R^2}\left(\frac{\partial A}{\partial\alpha}\right)^2 + \frac{C(\alpha)}{R} \tag{7}$$

where A is the action. The radius R is for the moment a constant, and all Coulomb interactions have been summarized by $C(\alpha)$, see (6). Therefore, this Hamilton function may be regarded as an adiabatic one. It controls radial correlation at constant values of the radius. Next, we remove that shortcoming.

To this end, we allow for a monotonous time-variation of the radius $R(t)$, *i.e.* $\dot{R} \neq 0$ that step leads us to a time-dependent Hamilton-Jacobi equation given by

$$H_{\text{adiabatic}}(A) = \frac{\partial A}{\partial t} \tag{8}$$

Since we do not know an explicit time dependence, we express the time t by the radius R using

$$\frac{\partial}{\partial t} = \dot{R}\frac{\partial}{\partial R} \tag{9}$$

Finally, we employ energy conservation on the ridge top given by

$$E = \frac{1}{2}\dot{R}^2 + \frac{C(\alpha_0)}{R} \tag{10}$$

We follow Wannier [2] and expect that transitions occur at radii R where the radial kinetic energy is equal to the potential on the ridge top.

This leads us to the following expression of $\dot{R}$

$$\dot{R} = \sqrt{-\frac{2C(\alpha_0)}{R}} \in \mathbb{R} \tag{11}$$

This velocity identifies above the ionization threshold a quantum wave number K Below threshold, we must replace the real K by the imaginary iK.

Along these lines, we arrive at the parabolic wave equation valid above threshold

$$\sqrt{-\frac{2c_0}{R}}\frac{\partial A}{\partial R} = H_{\text{adiab}}(A) \tag{12}$$

This resembles the inhomogeneous heat equation. The correspondence reads

$$\text{action} \Leftrightarrow \text{temperature}$$

$$\text{radius} \Leftrightarrow \text{time}$$

$$\text{angle } \alpha \Leftrightarrow \text{space coordinate}$$

$$\text{Coulomb interaction} \Leftrightarrow \text{external heat source}$$

That correspondence will be helpful for solving our parabolic equation.

Below the threshold, our parabolic differential equation reads

$$i\sqrt{\frac{-2c_0}{R}}\frac{\partial A}{\partial R} = \frac{1}{2R^2}\left(\frac{\partial A}{\partial \alpha}\right)^2 + \frac{C(\alpha)}{R} \tag{13}$$

An alternative derivation of (13) is given here. We start from the stationary Hamilton-Jacobi equation given by

$$\frac{1}{2}\left(\frac{\mathrm{d}A}{\mathrm{d}R}\right)^2 + \frac{1}{2R^2}\left(\frac{\mathrm{d}A}{\mathrm{d}\alpha}\right)^2 + \frac{C(\alpha)}{R} = E$$

We solve it with the Ansatz

$$A = KR + \sqrt{R}D(\alpha)$$

This leads directly to

$$\frac{K}{2\sqrt{R}}D + \frac{1}{8R}D^2 + H_{\text{adiabatic}} = 0$$

where we have used

$$\frac{1}{2}K^2 = E$$

and

$$K = i\sqrt{\frac{-2c_0}{R}}$$

to get (13). After multiplication with R, we arrive for the function $D(\alpha)$

$$i\sqrt{\frac{-c_0}{2}}D(\alpha) + \frac{1}{8}D^2 = \frac{1}{2}(D')^2 + C(\alpha) \tag{14}$$

with

$$c_0 = C(\alpha_0) < 0 \tag{15}$$

It is obvious that the solutions of (15) are imaginary. Therefore, we get an imaginary action, as may be expected below threshold.

4. Initial Value Problem and *S* Matrix

We now have all the ingredients to continue in quantum mechanics. Near its classical limit, the corresponding wave function is given by

$$\Psi(R,\alpha)=\exp\left[i\sqrt{R}D(\alpha)\right] \tag{16}$$

which is real in the classically forbidden region.

To employ (17) in an initial value problem [4], we need fundamental solutions. We expect that these depend strongly on the stationary point of $C(\alpha)$ and therefore of $D(\alpha)$. To this end, we approximate $D(\alpha)$ by

$$D(\alpha)=q_0-\kappa(\alpha-\alpha_0)^2 \tag{17}$$

We prefer to write the action in a real form and put

$$D(\alpha)=iF(\alpha)$$

Along these lines, we get two fundamental solutions of the form, see [4]

$$\Psi^{1,2}=\exp\left[-\sqrt{R}\kappa_{1,2}(\alpha-\alpha_0)^2\right] \tag{18}$$

with

$$\kappa_1(\alpha)=\sqrt{\frac{-c_0+19\lambda}{32}}+\sqrt{\frac{-c_0}{32}}>0 \tag{19}$$

$$\kappa_2(\alpha)=-\sqrt{\frac{-c_0+16\lambda}{32}}+\sqrt{\frac{-c_0}{32}}<0 \tag{20}$$

Distributions of the form (19) are well known as Fresnel distributions, and have the following properties

For $\kappa<0$

$$\lim_{R\to\infty}\exp\left(\sqrt{R}\kappa\alpha^2\right)\propto\delta(\alpha) \tag{21}$$

and

$$\lim_{R\to 0}\exp\left(\sqrt{R}\kappa\alpha^2\right)\propto\delta(\alpha-\alpha_0) \tag{22}$$

with $\alpha_0=\pi/4$, see [5].

But Fresnel distributions diverge for $\kappa>0$, see [6].

We are now ready to describe an excitation from an initial target state φ_i to a final state φ_f. We show how a transition occurs along the path through the lake of electron pairs.

To this end we start from an asymptotic initial state given by $R=\infty$ and $\alpha\approx 0$. The properly correlated incoming wave travels more strongly on the ridge top to the TCP at $R=0$ described by the converging solution with $\kappa_2<0$. In this way, the projectile electron pulls the target electron onto the ridge top, *i.e.*, the electron-electron interaction is attractive. We have here found a novel kind of

electron pairs. In contrast to Cooper pairs in superconductivity [3], the attraction emerges here from the nuclear Coulomb field rather than from lattice vibrations.

Reflection of our pair from the TCP leads to an unstable outgoing two-electron wave with action curvature $\kappa_1 > 0$ that leaves the ridge top and finally falls into a potential valley where all final target states are located. To get the S-matrix we must time-ordered connect the stable incoming wave with the diverging outgoing wave. Time order must be replaced by radius-order. Thus, we formally get the S-matrix

$$S = \Psi_1(\kappa_1) * \Psi_2(\kappa_2)$$

where the star stands for R-order.

5. Conclusions and Summary Matrix

For the first time, we have brought light into the details of electronic transitions, at least in the simplest case of only two electrons involved.

Our results are in conflict with the old but still often applied billiard model. The billiard model applies at ultrafast collisions, where correlation is negligible, but fails, however, at slower collisions. The Born model treats the electrons as mass points. We do it correctly and use matter waves. Thus, we observe electron wave diffraction, as Baptist Fresnel did more than 200 years ago with light.

We stress the absence of direct excitation. The path for excitation always goes through the lake of dominantly correlated electron pairs. Particularly important is the triple condensation point, which consists of a nucleus plus two dominantly correlated electrons. Electron-electron attraction in the incident channel leads to that surprising compound state. The arrival at the final state emerges from an unstable Fresnel distribution.

Concluding we remark that our present work will be extended shortly to many-electron atoms. We will then arrive at electron triples and further even n-tuples compound states of electrons, treated by corresponding generalized Fresnel distributions.

Finally, we remark that the subject under investigation opens an entirely new field of atomic matter. Experiments to demonstrate the electron-electron attraction are highly welcome.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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