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Insight into Electronic Transitions

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Abstract

We present a scattering theory for charged particles suitable for electron atom collisions. Starting from the Hamilton-Jacobi equation for N electrons in the field of a nucleus or an ion core, we derive a parabolic differential equation that resembles the heat equation. We identify a Fresnel distribution as the main ingredient of its kernel. In particular, we show that high multiply excited states are strongly suppressed increasingly so for approaching the ionization threshold. That effect compares favorably with experimental data. Also, the Wannier channel is controlled by a Fresnel distribution. Moreover, that channel represents a novel continuum to our knowledge that has never been considered so far. The classical action has been employed to derive quatum wave functions in the semiclassical limit. The curvature of the N-elctron potential surface is shown to be the essential ingredient of an initial value problem for elastic and/or inelastic processes. The spectral region near the ionization threshold needs a special action to describe the Wannier phenomenon. This Wannier channel manifests itself by a novel continuum never considered before.

Keywords

Many-Body Coulomb dynamics, Nonseparable Systems, Correlation, Wannier Phenomenon

1. Introduction

It is usually believed that the Schrödinger equation is an eigenvalue equation. It delivers energy levels and eigenfunctions but does not describe transitions. Actually, Heisenberg pointed out in the 30s [1] the need for a better wave equation in order to look into the details of transitions. Today, we can calculate transition probabilities, but the many-electron evolution during a transition remains still in the dark.

*Retired.

The aim of this paper is to present such an evolution equation for electron scattering from light atoms in non-relativistic approximation. The simplest example, electron scattering from hydrogen, is treated in detail for illustration. The generalization to more electrons is straightforward.

The paper is organized as follows. Section 2 discusses geometrical aspects and introduces the Hamilton-Jacobi equation for few-electron systems. In particular, we show that in the Coulomb zone, the classical action, in contrast to wave functions, separates into a product of two portions, each depending on one space coordinate only. Section 3 finally treats the quantum version in a semiclassical limit, and presents for the first time an evolution equation for fully correlated electron-atom scattering. The kernel of the evolution equation is shown to be closely related to the action. We identify this kernel as Fresnel distribution. The key quantity of that distribution is the curvature of the potential surface in its unstable two-electron equilibrium. Therefore, our kernel describes not only Wannier's threshold ionization but also transitions in other parts of the spectrum. Our wave equation formally resembles the heat equation. To this end, we treat the scattering process as an initial value problem [2]. We find unusual results like electron-electron attraction during transitions, a phenomenon generated by the diffraction of a correlated two-electron wave from a potential ridge. Moreover, we identify a hidden continuum in which the electrons move on top of a potential ridge.

Finally, Section 4 presents conclusions, an outlook and a summary. This section compares our development with the old Bethe theory [3], and mentions the applicability of our strategy to non-Coulomb systems.

2. Geometrical Apects and the Hamilton-Jacobi Equation for $H + e$

For the two-electron system consisting of one hydrogen atom plus one scattering electron, we express, following Wannier [4], the electron-nucleus distances by polar coordinates

$$\begin{aligned} r_1 &= R\sin\alpha \\ r_2 &= R\cos\alpha \end{aligned} \tag{1}$$

with the radius

$$R = \sqrt{r_1^2 + r_2^2} \tag{2}$$

and the pseudo-angle

$$\alpha = \tan^{-1}\frac{r_1}{r_2} \tag{3}$$

with $0 < \alpha < \pi/2$.

The generalization to more, say N, dominantly correlated electrons is straightforward. Then, we put these electrons onto a sphere $\mathbb{S}_N$ of dimension N; thus, each electron has one radial degree of freedom.

Using the above coordinates, the electrostatic potential energy reads for single excitation in non-relativistic approximation for two-electron systems

$$V = \frac{C(\alpha)}{R} + \frac{1}{r_{12}} \tag{4}$$

with the charge function given by

$$C(\alpha) = -\frac{Z}{\sin\alpha} - \frac{Z}{\cos\alpha} = -2\sqrt{2}Z\frac{\cos(\alpha - \pi/4)}{\sin 2\alpha} \tag{5}$$

and r_{12} is the electron-electron separation, Z is the nucleus charge.

The stationary Hamilton Jacobi equation for N electrons on the sphere reads, then

$$\frac{1}{2}\left(\frac{\partial A}{\partial R}\right)^2 + \frac{1}{2R^2}(grad\,\omega)^2 + \frac{C(\omega)}{R} + \sum_{i<j}^{N}\frac{1}{r_{ij}} = E \tag{6}$$

where A is the action, ω stands for the set of angles necessary to parametrize the sphere, R is the sphere radius, the charge function reads

$$C(\omega) = ZR\sum_{i=1}^{N}\frac{1}{r_i} \tag{7}$$

and the sum in Equation (6) summarizes all electron pairs.

Our treatment uses a sphere Σ_N of dimension N for N electrons, rather than a Cartesian space. To this end, we put all electrons on a sphere with a radius given by

$$R^2 = \sum_{i=1}^{n} r_i^2 \tag{8}$$

The gradient in Equation (6) acts only on the surface of the sphere, A is the action, E is the total energy and ϑ is the solid angle between the two electron direction vectors.

Standard scattering theories decompose the total configuration space into two subspaces, namely, a reaction zone plus a free zone. In a scattering process, the projectile starts from a free zone, penetrates into the reaction zone and escapes again into a final free zone. That picture cannot be used in the case of long-range Coulomb forces. Short-range energy terms in Equation (6) scale with $1/R^{-2}$ whereas the Coulomb terns scale with $1/R$. We now reduce Equation (6) to the Coulomb zone. The gradient term seems to belong to the reaction zone, but that is not always true, as we will see below.

We treat now the two-electron problem in the Coulomb zone, whereas the reaction zone needs a numerical treatment. The repulsion terms in Equation (6) must also be in the reaction zone because they depend on angles and couple, therefore, to centrifugal terms.

In the case of single electron excitation, we arrive at

$$\frac{1}{2}\left(\frac{\partial A}{\partial R}\right)^2 + \frac{1}{2R^2}\left(\frac{\partial A}{\partial \alpha}\right)^2 + \frac{C(\alpha)}{R} = E \tag{9}$$

where α and $C(\alpha)$ are given by Equations (3) and (5).

To solve Equation (9), we decompose the action into two terms,

$$A(R,\alpha) = KR + \Pi(R,\alpha) \tag{10}$$

where the first term KR describes free electrons and the second one Π is responsible for Coulomb corrections, including correlation, and also for a transfer of kinetic energy into potential energy. Substitution of Equation (10) into Equation (6) yields, restricted to the Coulomb zone,

$$\frac{1}{2}\left(K+\frac{\partial\Pi(R,\alpha)}{\partial R}\right)^2+\frac{1}{2R^2}\left(\frac{\partial\Pi}{\partial\alpha}\right)^2+\frac{C(\alpha)}{R}=E \quad (11)$$

The squared radial momentum above identifies the total energy

$$\frac{1}{2}K^2=E \quad (12)$$

In addition, we find in Equation (11) a cross-term given by

$$K\frac{\partial\Pi}{\partial R} \quad (13)$$

This term destroys the separability of interacting many-body systems (three or more bodies). We will see shortly that this cross-term produces a transfer of kinetic energy into potential energy and vice versa. In this way, we give up the validity of a virial theorem. There are two sorts of action (below denoted by Type 1 and Type 2) to transfer momentum into potential Coulomb energy:

Type 1:

$$\Pi(R,\alpha)=A(\alpha)\ln R \quad (14)$$

Type 2:

$$\Pi(R,\alpha)=B(\alpha)\sqrt{R} \quad (15)$$

The Type 1 cross-term causes an additional contribution to the Coulomb zone, which may be combined with the static potential, *i.e.*,

$$K\frac{\partial\Pi}{\partial R}+\frac{C(\alpha)}{R}=\frac{KA(\alpha)+C(\alpha)}{R} \quad (16)$$

Thus, we observe in Equation (16) an energy-dependent Coulomb interaction different for incoming/outgoing waves depending on the sign of the momentum K. Below the threshold, we replace K by $\pm i\Upsilon$ We expect that these Type 1 channels apply for electron locations in the attractive regions of the charge function $C(\alpha)$. It is surprising that the charge function alone determines observable data. We stress that a gradient actually enters. The gradient, however, creates a force. In both cases, Types 1 and 2 are located on the sphere.

The case Type 2 applies if the correlated two-electron charge distribution is mainly located on top of the charge function, which occurs near $\alpha=\pi/4$ where $C(\alpha)$ has a local maximum. The charge function has, therefore, on its top the

[1]Our Taylor approximation differs from Wannier's. He tries to expand the potential at the point $\alpha=\frac{\pi}{4}$ and $\vartheta=\pi$. The potential surface, however, is, at that point, **not** a C^∞ function. There is no environment in which each Cauchy sequence converges to that point. Our function $C(\alpha)$ circumvents that problem.

Taylor approximation[1].

$$C(a)=\lambda+\kappa\left(\alpha-\frac{\pi}{4}\right)^{2} \tag{17}$$

The region $\alpha\cong\frac{\pi}{4}$ includes the ionization threshold region, but not only that, as we will see below. In the case of Type 2 it would be too naiv to use in Equation (13) simply the threshold value $K=0$. To take a broader region near the threshold into account, we follow Wannier [4] and consider the region $\alpha\cong\pi/4$ which includes the ionization threshold region, but not only that, as will be seen below. In the case of Type 2, it would be too naive to use Equation (13) simply the value $K = 0$. To take a broader region near the threshold into account too, we follow Wannier [4] and consider the classical energy conservation provided the electrons are located on the top of $C(\alpha)$,

$$E=\frac{K^{2}}{2}+\frac{\lambda}{R} \tag{18}$$

see Equation (17).

At $E\approx0$ we get

$$K(0)\approx c\sqrt{-\frac{2\lambda}{R}} \tag{19}$$

with $\lambda<0$. Thus, we find now in the Coulomb zone one more Coulomb contribution given by

$$K\frac{\partial\Pi}{\partial R}=B(\alpha)\sqrt{-\frac{\lambda}{2}}\frac{1}{R} \tag{20}$$

3. Quantum Version

To put our classical results of Section 2 into quantum mechanics, we put our action A into an exponential

$$G(R,\alpha)=\exp\{iA(R,\alpha)\} \tag{21}$$

This function G, also referred to as kernel, serves to define an initial value problem provided the following two conditions are fulfilled:

(i) G must be a solution of Equation (11);

(ii) G must converge to a delta function, *i.e.*,

$$\lim_{R\infty}G(R,\alpha-\alpha')\propto\delta(\alpha-\alpha') \tag{22}$$

For the action of Type 1, condition #1 is evident. The convergence Equation (22) may be seen as follows. We consider integrals of the form

$$I=\int_{0}^{\pi/2}\mathrm{d}\beta'\exp\left\{if(R)(\beta-\beta')^{2}\right\}T(R,\beta') \tag{23}$$

where $f(R)>0$ and $\lim_{R\infty}f(R)=\infty$ and T is any trial function such that the integral exists. In Equation (23), we integrate a rapidly oscillating function for large values of the function $f(R)$ except if $|\beta-\beta'|$ is close to zero. Then, the integral converges to a delta function according to the formula

$$\lim_{\varepsilon\to 0}\exp\left[\frac{i}{\varepsilon}c\left(\beta-\beta'\right)^2\right]\propto\frac{1}{\sqrt{c}}\delta\left(\beta-\beta'\right) \tag{24}$$

see [5]. We use for Type 1 $\varepsilon = 1/\ln R$ and $c = -1/\Gamma > 0$. The integral converges for incoming waves $\Gamma < 0$, and delivers a wave function at any point (R,β). If T is an asymptotic state at ($R=\infty$, $\beta'\approx 0$), we observe for decreasing values of R *an* excitation onto the top of the ridge near $\alpha - \pi/4 \approx 0$.

We now apply the above technique to the whole action $A(R,\alpha)$ and employ either $f(R) = \ln R$ or $\sqrt{R}$. Thus, we finally get the Type 1 kernel

$$G\left(R,\beta-\beta'\right)=exo\left\{i\left(\frac{K\ln R}{K}\right)\left(\beta-\beta'\right)^2\right\} \tag{25}$$

This compares favorably with the Fresnel representation of the delta function

$$\delta\left(\alpha-\alpha'\right)=\lim_{\varepsilon\to+0}\frac{1}{\sqrt{i\pi\varepsilon}}\exp\left\{\frac{i\left(\alpha-\alpha'\right)^2}{\varepsilon}\right\} \tag{26}$$

with $\epsilon = 1/\ln R$, see [5]. Thus, our kernel converges indeed to $\propto\delta\left(\alpha-\alpha'\right)$. We stress, however, that this conclusion is valid only for positive imaginary exponents. If this is the case, the incoming two-electron charge distribution converges to the Wannier point $\beta = 0$. For an outgoing wave, the Fresnel integral diverges. Consequently, the flux leaves the top of the ridge, falling into attractive potential regions and creating an excited H atom.

Below the threshold, we must replace the wave number K by $\pm i\Upsilon$ with $\Upsilon\in\mathbb{R}$. This leads to a real Fresnel distribution, also known as a normal distribution [5] with $K = -i\Upsilon$. The exponent in Equation (25) is then negative real and leads for small values of Υ to a strong exponential suppression of high Rydberg resonances slightly below the threshold as observed by [6]. That suppression has nothing to do with the Wannier phenomenon. However, Type 2 action also predicts an intensity suppression at high double excitation. Because the ionization cross section shows a potential law near the threshold, one might expect the Type 2 action to also have a potential slope below the threshold. Only highly accurate experimental data better than [6] (presently not available) could distinguish between these two mechanisms.

Also, the Type 2 action leads to a Fresnel distribution, Equation (25) must now be replaced by

$$G\left(R,\alpha-\alpha'\right)=\exp\left\{i\sqrt{R}\Gamma\left(\alpha-\alpha'\right)^2\right\} \tag{27}$$

where Γ is the curvature of the Type 2 action.

In contrast to the Type 1 case, we now get converging evolutions in both incoming and outgoing directions. That identifies a hidden collision channel stemming from dominant correlation. This channel manifests itself in the Wannier law for threshold ionization and in its unexpected range of validity. We expect this Type 2 channel to be active also below the threshold. All single-electron excitations must be embedded into that Type 2 continuum before comparing with experimental data. The embedding procedure will be subject of another publication.

4. Conclusions and Summary

We have presented the frame of a scattering theory for electron atom collisions, including correlation. For that goal, we have developed a novel parabolic partial differential equation, which manifests itself as an initial value problem. For the purpose of illustration, we have applied that equation to the electron hydrogen system.

For the first time, we have found a unique treatment for the whole spectrum that is limited to non-relativistic energies. We have exactly calculated the kernel of our wave equation. That is closely related to the curvature of the two-electron potential surface. Our kernel manifests itself as Fresnel distribution. As long as the electrons are located away from a stationary configuration, we get a kernel parameter that describes stable incoming flux converging to the Wannier point. After reflection from the nucleus, the two-electron wave becomes unstable and leaves the potential ridge. The final state consists of one escaping electron plus one target bound state. Our initial value treatment allows, for the first time, the details of the two-electron charge distribution to be looked into at any stage of the transition.

The case denoted in this article as Type 1 constitutes a generalization of Bethe's treatment, except that our work applies not only to fast collisions, and we use a better phase denoted by Π in this article. Actually, we fall back to Bethe if we disregard any correlation and employ a one-electron Coulomb phase Π as target action.

The Type 2 solution is a novelty in atomic physics. Here, we get a stable wave propagation along the potential ridge in both directions. This wave mode creates a continuum to our knowledge that has never been considered before.

According to our analysis, this mode is much more than a threshold phenomenon since doubly excited Rydberg states are degenerate in that continuum. This requires an embedding of these states into that continuum. That aspect has never been considered so far.

At first glance, it seems surprising that two types of action are needed to cover the whole spectrum. There is, however, a huge difference between these two Types. Type 2 enters the gradient of the charge function, whereas in Type 1, only the function value itself is entered. The gradient of the charge functions as an ingredient of the potential energy and creates a force. That hidden force is energy-dependent and manifests itself primarily in the threshold region.

This necessary embedding mentioned above is sub-satanically different from Fano's [7] embedding of one bound state into one single electron continuum.

We have the feeling that unstable particle configurations generally constitute the key to transitions. Consider, for instance, two fragments (for example, atoms or nucleons) outside a molecule or nucleus. Assume a potential description of the whole complex of the form

$$V = U(r_1) + W(r_2).$$

That potential field V has always a stationary configuration. This is immediately obvious if we employ polar coordinates, see our Equation (1), and differentiate,

$$\frac{dV}{d\alpha} = U'(R,\alpha)\cos\alpha - W'(R,\alpha)\sin\alpha$$

which has a zero at

$$\alpha = \tan^{-1}\frac{U'(R,\alpha)}{W'(R,\alpha)}$$

It is obvious that transitions in all spectral regions are controlled by the curvature of the corresponding potential surface.

Our strategy also serves to amend the Born-Oppenheimer approximation [8], a standard in molecular physics for many decades. [9] calculates eigenvalues of an adiabatic Hamiltonian, $H_{adiab}(R,\omega)$ where R is the nucleus-nucleus separation in a diatomic molecule and ω stands for all electronic coordinates. Our treatment replaces the eigenvalue problem with an evolution equation by treating the internuclear separation R for the moment as a classical time-dependent coordinate $R(t)$, and applying the time-dependent wave equation $H_{adiab}(R,\omega)\Psi = i\frac{\partial\Psi}{\partial t}$. Finally, we eliminate the time t by using the chain rule $\frac{\partial}{\partial t} = \dot{R}\frac{\partial}{\partial R} = K\frac{\partial}{\partial R}$ and arrive at our evolution equation.

Also, in huge macromolecules (often relevant in medicine, biology and pharmacy), electronic equilibria may be important for reactions. The potential energy of such molecules shows many equilibria. We believe that targeted manipulations of huge molecules may become possible, provided some information about the molecular structure in a multidimensional space is available. We expect their structure to be the basis of molecular properties and intrinsic reactions. This study may be a step toward targeted manipulations of macromolecules.

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Conflicts of Interest

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

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