

# Dominant Correlation Effects in Atomic Spectra

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**Abstract**—High double excitation of two-electron atoms has been investigated using hyperpherical coordinates within a modified adiabatic expansion technique. This modification creates a novel fictitious force leading to a spontaneous exchange symmetry breaking at high double excitation. The Pauli principle must therefore be regarded as approximation valid only at low excitation energy. Threshold electron scattering from high Rydberg states shows an unexpected time reversal symmetry breaking. At threshold for double escape we discover a broad (few eV) Cooper pair.

**Keywords**—Correlation, resonances, threshold ionization, Cooper pair.

## I. INTRODUCTION AND PREVIOUS WORK

THE simplest atom which allows correlation phenomena is the two-electron atom like *He*. We consider here helium-like atoms with the Hamiltonian in nonrelativistic approximation given by (in a. u.)

$$H = -\frac{1}{2}(\Delta_1 + \Delta_2) + V(\vec{r}_1, \vec{r}_2) \quad (1)$$

where  $\vec{r}_1, \vec{r}_2$  are the electron position vectors with respect to an infinitely heavy nucleus, the potential is given by

$$V = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad (2)$$

where  $Z$  is the nuclear charge.

The Hamiltonian commutes with three trivial symmetry operations: Parity, electron exchange and overall rotations. Common eigenstates of energy, spin, parity and orbital angular momentum exist.

Single-electron coordinates are not suitable to study correlation phenomena. In this paper we consider the charge cloud as a whole, and employ the quantity  $R$  related to the trace of the inertia tensor  $I$

$$R = \left(\frac{1}{2} \text{tr} I\right)^{\frac{1}{2}} = \sqrt{r_1^2 + r_2^2} \quad (3)$$

as collective coordinate. Alternatively, this coordinate may be considered as radius of a five-sphere  $S_5 \in R_6$  because the position space of both electrons has dimensioned six i.e. each point on  $S_5$  represents one electron pair configuration. We simplify further the problem by restricting ourselves at the

moment to pure S-states. To eliminate overall rotations we cut out a three-sphere from the five-sphere. Thus we arrive at a two-sphere  $S_2 \in R_3$ . One point on this  $S_2$  stands for a non-rotating two-electron configuration. The radius of  $S_2$  is equal to  $R$  given by (3). Now we introduce polar angles on  $S_2$ . To this end we consider the tensor of inertia in its diagonal form

$$I = R^2 \begin{pmatrix} \sin^2 \psi & 0 & 0 \\ 0 & \cos^2 \psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (4)$$

with  $R$  given by (3). The parametrisation (4) takes into account the relation  $I_{xx} + I_{yy} = I_{zz}$  valid for plane bodies.

Here we have put the body-fixed x-axis into the direction of the smallest principal moment of inertia. The angle  $\psi$  is therefore limited by  $0 \leq \psi \leq \frac{\pi}{4}$ . The physical meaning of this angle is the asymmetry of the inertia given by

$$\cos 2\psi = \frac{I_{yy} - I_{xx}}{I_{zz}} \quad (5)$$

The geometrical meaning of this angle is easy:  $\psi = 0$  describes all collinear configurations, whereas  $\psi = \frac{\pi}{4}$  corresponds to symmetric tops. Between these two values we find all asymmetric tops. We restrict here the angle  $\psi$  to positive values. This corresponds to the northern hemisphere of the full two-sphere. The full  $S_2$  would double count all 2-electron configurations. Equation (4) shows clearly that a negative  $\psi$  leads to the same inertia. Here we employ this angle  $\psi$  as latitude on the hemisphere. For a complete description we need one further angle as azimuth. This may be chosen as

$$\tan \varphi = \frac{r_1^2 - r_2^2}{2(R^2 - r_{12}^2)} = \frac{r_1^2 - r_2^2}{4\vec{r}_1 \cdot \vec{r}_2} \quad (6)$$

The mapping from the hemisphere to the body-fixed frame reads [1]

$$\vec{r}_i = R \begin{pmatrix} \cos \psi \cos \frac{1}{2}(\varphi + \beta_i) \\ \sin \psi \sin \frac{1}{2}(\varphi + \beta_i) \\ 0 \end{pmatrix} \quad (7)$$

with  $\beta_1 = \frac{3\pi}{2}$  and  $\beta_2 = -\frac{3\pi}{2}$ . These and similar hyperspherical coordinates have been described elsewhere [2];

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they have been used in the context of several three-body problems [3].

The Hamiltonian for a helium-like atom reads in the above introduced coordinates

$$H = -\frac{1}{2}R^{-5} \frac{\partial}{\partial R} R^5 \frac{\partial}{\partial R} + \frac{\Lambda^2}{2R^2} + \frac{C(\psi, \varphi)}{R} \quad (8)$$

where  $\Lambda^2$  generates rotations on the hemisphere and is given by:

$$\Lambda^2 = -\frac{1}{\sin 4\psi} \frac{\partial}{\partial \psi} \sin 4\psi \frac{\partial}{\partial \psi} - \frac{4}{\cos^2 2\psi} \frac{\partial^2}{\partial \varphi^2} \quad (9)$$

The charge function  $C(\psi, \varphi)$  is given by

$$C(\psi, \varphi) = RV = -\frac{Z\sqrt{2}}{\sqrt{1-\cos 2\psi \sin \varphi}} - \frac{Z\sqrt{2}}{\sqrt{1+\cos 2\psi \sin \varphi}} + \frac{1}{\sqrt{1-\cos 2\psi \cos \varphi}} \quad (10)$$

Reference [1] has constructed eigenfunctions and energy eigenvalues following a Born-Oppenheimer –method [1], [4]. We search at first a basis of angular functions at constant values of  $R$ , i.e. we solve the eigenvalue problem

$$\left[ \frac{\Lambda^2}{2R^2} + \frac{C(\psi, \varphi)}{R} \right] \Phi_\mu(\psi, \varphi; R) = U_\mu(R) \Phi_\mu(\psi, \varphi; R) \quad (11)$$

The eigenvalues  $U_\mu(R)$  may be regarded as  $e - He^+(n, l)$  potentials, correlation taken into account. Their asymptotic behaviour reads:

$$U_\mu(R) \rightarrow -\frac{Z^2}{2n^2} - \frac{Z-1}{R} \quad (12)$$

In a second step energy eigenvalues are obtained by solving the radial equations

$$\left[ -\frac{1}{2}R^{-5} \frac{d}{dR} R^5 \frac{d}{dR} + U_\mu \right] F_\mu(R) = EF_\mu(R) \quad (13)$$

The total wave function has then the product form  $\Psi_\mu(R, \psi, \varphi) = F_\mu(R) \Phi_\mu(\psi, \varphi; R)$ . This product form introduces an approximation. We have neglected non-adiabatic coupling terms.

Along the above lines many singly and doubly excited states have been accurately calculated [1]. The results compare favourably with other theoretical and with experimental data. However, for increasing excitation energy our results become less and less accurate. Near the threshold for double escape this description breaks even down. It is the purpose of this paper to repair this shortcoming.

## II. NEW DEVELOPMENT

We believe that the above BO-like description needs an improvement. The unusual quantity in this treatment is the

operator  $\Lambda^2$ . It constitutes at small values of  $R$  a centrifugal barrier to avoid a collapse of the whole atom. Reference [1], however, has overlooked that this operator changes at larger  $R$ -values the Coulomb potentials. This circumstance is slightly hidden, but may be seen as follows.

We multiply the lhs of (11) with a smooth test function  $\Xi$  and integrate over the hemisphere  $H$

$$\int_H \Xi \left( \frac{\Lambda^2}{2R^2} + \frac{C(\psi, \varphi)}{R} \right) \Phi R^2 \sin 4\psi d\psi \wedge d\varphi \quad (14)$$

and assume smoothness in the sense  $|\vec{\nabla} \Xi| \ll |\Xi|$  and  $|\vec{\nabla} \Phi|$  may be bounded on  $H$ . Modern differential geometry, see e. g. [5] identifies  $\Lambda^2$  as a Cartan derivative of a vector field given by  $-\vec{\nabla} \Phi$ .

Stokes theorem [5] converts then the first integral in (14) into a line integral of this vector field  $-\vec{\nabla} \Phi$  along the boundary  $\partial H$  of the hemisphere. That boundary is simply the equator located at  $\psi = 0$ . The quantity under consideration (14) may therefore be rewritten as

$$\int_{\partial H} \Xi \left( \frac{-\vec{\nabla}}{2R^2} \right) \Phi R d\varphi + \int_H \Xi \left( \frac{C(\psi, \varphi)}{R} \right) \Phi R^2 \sin 4\psi d\psi \wedge d\varphi \quad (15)$$

This last step has neglected the gradient-gradient-coupling  $(\vec{\nabla} \Xi) \cdot (\vec{\nabla} \Phi)$ . The two integrals in (15) may be put into one single one with help of a delta function, i.e. we arrive at

$$\int_H \Xi \left( \frac{-\delta(1-\cos 4\psi) \vec{\nabla}}{2R^2} \right) \Phi R^2 \sin 4\psi d\psi \wedge d\varphi + \int_H \Xi \frac{C(\psi, \varphi)}{R} \Phi R^2 \sin 4\psi d\psi \wedge d\varphi \quad (16)$$

This must hold for any smooth test function  $\Xi$ , we therefore conclude that the static potential should be replaced by:

$$C(\psi, \varphi) \Rightarrow C(\psi, \varphi) - \frac{\delta(1-\cos 4\psi)}{R} \vec{\nabla} \quad (17)$$

The gradient on the hemisphere is given by:

$$\vec{\nabla} = \frac{1}{R} \left( \hat{e}_\psi \sin 4\psi \frac{\partial}{\partial \psi} + \hat{e}_\varphi \frac{2}{\cos 2\psi} \frac{\partial}{\partial \varphi} \right) \quad (18)$$

which simplifies on the equator ( $\psi = 0$ ) to

$$\hat{e}_\varphi \cdot \vec{\nabla} = \frac{2}{R} \frac{\partial}{\partial \varphi} \quad (19)$$

The effective interaction within the three-body complex reads therefore;

$$\bar{C} = C(\psi, \varphi) - \frac{2}{R^2} \delta(1 - \cos 4\psi) \frac{\partial}{\partial \varphi} \quad (20)$$

Equation (20) is the main result of this section. We stress that the replacement (20) has emerged mainly from intuition rather than from a rigorous derivation. However, it appears plausible that it may repair the BO shortcoming observed in [1]. We will see in the next section that calculations performed using (20) compare favourably with high precision experimental data. However, this modification of the pure Coulomb potentials looks unusually, and requires some immediate comments. It constitutes a fictitious force and has nothing to do with electrostatics. In contrast to classical fictitious forces like centrifugal or Coriolis force our fictitious force is a pure quantum effect and emerges from the diffraction of an electron wave from a three-body potential surface. The derivative term  $\frac{\partial}{\partial \varphi}$  constitutes except for an imaginary factor of  $i$  the momentum conjugate to the radial correlation coordinate  $\varphi$ . We expect therefore that (20) disturbs the shell structure of the atom, or even destroys the shells. Closely related to the shell structure is the Pauli principle. Electron exchange is described in our coordinates by the replacement  $\varphi \rightarrow 2\pi - \varphi$ , all other coordinates unchanged.

The odd derivative term  $\frac{\partial}{\partial \varphi}$  prevents singlet and triplet channels. This, however, is not in contradiction to the observation of lower resonances and to other standard theoretical work. We remark that the BO method, see (11), calculates standing wave solutions in two dimensions. These channel wave functions are equal to zero on the equator, similar like the transverse elongation of a vibrating membrane on the boundary. The fictitious force does therefore not contribute. This argument applies to the ground channel and to lower excited channels where resonances may be regarded as bound states in a continuum. The situation, however, changes drastically at extremely high double excitation, a largely unknown spectral region so far, where the improved channel equation

$$\left( \frac{\Lambda^2}{2R^2} + \frac{\bar{C}}{R} \right) \Phi = U(R)\Phi \quad (21)$$

$$\left[ -\frac{1}{2R^2} \frac{\partial}{\psi} \frac{\partial}{\psi} - \frac{1}{2R^2} \frac{\partial^2}{\partial \varphi^2} - \frac{\delta(1-8\psi^2)}{R^2} \frac{\partial}{\partial \varphi} - \frac{C_0}{R} + \frac{C_1}{2R} \psi^2 - \frac{C_2}{2R} (\varphi - \pi)^2 \right] \Phi_\infty = U_\infty \Phi_\infty \quad (24)$$

Equation (24) can be solved by separation. To this end, we put:

$$\Phi_\infty(\psi, \varphi; R) = g(\psi; R)h(\varphi; R) \quad (25)$$

and start with the normalized portion  $g(\psi; R) = \sqrt{b} \exp(-b\psi^2)$ . This normalization is approximate.

calculates now travelling waves describing  $e - He^+$  scattering. As long as incoming and outgoing waves emerge from the same potential we fall back to shell structure and Pauli principle because the travelling waves can be combined to standing waves. Otherwise, we arrive at an unexpected spontaneous exchange symmetry and time reversal symmetry breaking. It is astonishing that a simple system like the He-atom shows such phenomena. We remark also that (20) is not Hermitian. Eigenvalues of (21) are therefore not necessarily real. The following example, the equator channel will demonstrate this phenomenon. The imaginary parts of the potential eigenvalues may be different for incoming and outgoing waves. Complex eigenvalues are not astonishing. An alternative treatment based on a rotation in phase space also led to complex eigenvalues [6].

### III. EQUATOR CHANNEL

The fictitious force becomes most important at extreme double excitation, i.e. near the threshold of double escape.  $e - He^+$  scattering occurs then mostly near the equator. The equator contains all two-particle coincidence configurations, but also the very important Wannier point where the electrons are at equal distances and in opposite directions from the nucleus. In the neighbourhood of this point we now solve exactly the modified channel equation (21). To this end we use a Taylor expansion of the function  $C(\psi, \varphi)$

$$C(\psi, \varphi) = -C_0 + \frac{1}{2} C_1 \psi^2 - \frac{1}{2} C_2 (\varphi - \pi)^2 \quad (22)$$

with the coefficients

$$C_0 = \frac{4Z-1}{\sqrt{2}}, C_1 = \frac{1}{\sqrt{2}}, C_2 = \frac{12Z-1}{\sqrt{2}} \quad (23)$$

The new channel equation reduces near the Wannier point to:

Instead of  $\int_0^{\frac{\pi}{4}}$  we have used  $\int_0^\infty$  which hardly changes the result. Then we find  $b = \sqrt{\frac{C_1 R}{2}}$  and a contribution to the

eigenvalue  $\frac{4b}{2R^2} = \sqrt{\frac{C_1}{2}} R^{-\frac{3}{2}}$ . The function  $h(\psi; R)$  is less trivial. A convenient starting point reads

$$h(\varphi; R) = \exp\left[\pm i\sigma(\varphi - \pi)^2 + \tau(\varphi - \pi)\right] \quad (26)$$

We average (24) over  $\psi$ , substitute (26) into (24) and calculate the parameters  $\sigma$  and  $\tau$ . Thus, we arrive at

$$\sigma(R) = \sqrt{\frac{C_2 R}{2}} \quad \text{and} \quad \tau = -\sqrt{\frac{C_1 R}{8}} \quad (27)$$

The plus sign in (26) describes an outgoing wave along the antioscillator coordinate  $\varphi$ , whereas the minus sign stands for an incoming wave. Therefore, we find two complex conjugate potentials given by

$$U_{\infty}^{\pm}(R) = \frac{15}{8R^2} - \frac{C_0}{R} + \left( \sqrt{\frac{C_1}{2}} \mp i\sqrt{\frac{C_2}{2}} \right) R^{-\frac{3}{2}} \quad (28)$$

Equation (28) consists of a centrifugal barrier plus an attractive Coulomb potential for the electron pair as a whole plus a complex contribution stemming from the potential ridge curvature. The imaginary part occurs if and only if there is an antioscillator portion at the saddle point. Equation (28) shows clearly  $ImU = 0$  occurs only if the potential curvature  $C_2 = 0$ . This is an exact result within this framework.

The zero-energy radial function may be represented also by a phase. To this end we write

$$F_{\infty}(R) = e^{iS(R)} \quad (29)$$

with the ansatz

$$S = A\sqrt{R} + B \ln R \quad (30)$$

We find for large  $R$  (up to the power  $R^{-\frac{3}{2}}$ )  $|A| = \sqrt{8C_0}$  and  $B$  may be obtained from the relation  $B = A^{-1}(\sqrt{2C_1} \mp i\sqrt{2C_2})$  valid for  $|A| \gg \frac{1}{8}$ . Obviously the quantity  $B$  depends on the sign of  $A$ , and is therefore different for incoming and outgoing flux along  $R$ .

We treat at first the outgoing wave, i.e. we put  $A^{out} = +\sqrt{8C_0}$ , and arrive at  $B^{out} = -\sqrt{\frac{C_1}{4C_0}} \pm i\sqrt{\frac{C_2}{4C_0}}$ . Now we must assign one of the two waves along  $\varphi$  to the outgoing  $R$ -flux. The above value  $B^{out}$  produces a factor of  $e^{iB^{out} \ln R} = R^{\mp\mu_0}$  to the radial wave function, with

$$\mu_0 = \sqrt{\frac{C_2}{4C_0}} \quad (31)$$

Near the threshold for double escape the radial wave function depends only through the combination  $KR$  with  $K = \sqrt{2|E|}$  on the energy. The ionization cross section would therefore show the behaviour  $\sigma \propto E^{\mp\mu_0}$ . The upper sign is entirely unrealistic, because this predicts a singular threshold cross section. Actually the cross section shows a power behaviour like  $\sigma \propto E^{\mu}$ , see [7] and [8]. We stress, however, that our  $\mu_0$  is not identical to Wannier's  $\mu$  because we employ here an adiabatic quantum approach whereas Wannier has an exact classical solution. Nevertheless, the experiment selects here the outgoing  $\varphi$ -wave to be combined with the outgoing  $R$ -wave. Moreover, this choice correctly predicts a cusp in the excitation cross section as observed in [8]. With this assignment we conclude that the incoming  $\varphi$ -wave combines with the incoming  $R$ -wave. This incoming wave shows then an amplification factor  $R^{-\mu_0}$  valid for decreasing  $R$ -values.

The results of this § may be summarized as follows. Near threshold for double escape we find two solutions. One incoming wave describing  $e-H$  or  $e-He^+$  scattering. This solution corresponds to Wannier's [7] converging trajectory, i.e. due to the fictitious force the incoming wave front is turned towards to the top of the potential ridge. The electrons move then in opposite direction and equal distance from the nucleus. Apparently in this mode of motion the electrons attract each other. Electron pairs with that property are usually referred to as a Cooper pair [9]. A centrifugal barrier avoids the collapse of the whole complex. The pair is reflected at this barrier sphere and performs now an outgoing wave. The fictitious force is now repulsive. The electrons leave the ridge and the Cooper pair decays. This motion corresponds to Wannier's diverging solution. From this viewpoint electron impact ionization near threshold may be regarded as decay of a Cooper pair. Slightly below threshold, however, the expanding complex experiences an outer turning surface given by the potential component  $-\frac{C_0}{R}$ . Reflection there transforms the outgoing wave again into an incoming one which blows up the lifetime of the Cooper pair. In contrast to a Fano resonance profile [10] the bare Cooper resonance profile reads simply  $\sigma \propto |E - E_0|^{\mu_0}$  where  $E_0$  is the ionization threshold.

So far, we have treated only  $S$ -states corresponding to zero angular momentum. The important equator channel remains however unchanged for rotating atoms. In our coordinates, there occurs a rotation-vibration-coupling like in molecules. This coupling occurs in the kinetic energy and is here given by

$$\frac{4 \sin 2\psi}{\cos^2 2\psi} \frac{\partial^2}{\partial \varphi \partial \gamma} \quad (32)$$

see (6) of [1]. Here  $\gamma$  is the rotation angle around the body-fixed  $z$ -axis. Equation (32) shows clearly the this coupling disappears on the equator  $\psi = 0$ .

## IV. GEDANKEN EXPERIMENT

Let us here consider a linear chain of atoms, all in high Rydberg states. We hit now one atom by a slow electron. This electron is attracted by this Rydberg electron due to the fictitious force, and forms Cooper pair. After reflection of the pair at the inner turning sphere the pair decays due to the repulsive fictitious force. The pair leaves the potential ridge, and one electron escapes. During the decay it experiences the repulsive fictitious force. However, as soon as it approaches the next neighbour atom the electron moves in the incoming wave mode, and the e-e interaction becomes attractive. Thus a new Cooper pair is born. This alternating sequence of production and decay of Cooper pairs may occur through the whole chain. The macroscopic observer will see one Cooper pair travelling along the chain.

## V. SUMMARY

The structure of resonance spectra close to an ionization threshold has been a mystery for a long time. A naïve consideration might expect infinity of double Rydberg states, so called planetary states where both electrons move on circular orbits. This picture, however, is oversimplified. We have shown that these double Rydberg states are suppressed by a novel fictitious force. This fictitious force has only little influence on bound states and lower resonances which may be regarded as bound states in a continuum. At increasing excitation energy, however, the fictitious force becomes more and more important, and leads to unexpected effects. We have shown that in this upper part of the resonance spectrum the exchange symmetry is spontaneously broken i.e. the total spin is not conserved, and therefore the shell-model including the Pauli principle is violated. Moreover, e-He<sup>+</sup> and e-H(nl) scattering violate time reversal symmetry. At threshold for double escape we discover the formation of a Cooper pair. This manifests itself in slow electron scattering from a Rydberg state. In the incoming wave mode, the two electrons attract themselves due to the fictitious force. After reflection on an inner turning sphere this force becomes repulsive in the outgoing wave, and the pair decays. For the Cooper pair we find modified time reversal symmetry. The Cooper wave function carries an index  $\mu_0$  depending on the potential surface curvature. Time reversal is then provided by complex conjugation as usual but combined with the replacement  $\mu_0 \rightarrow -\mu_0$ ,

$$T\Psi(R,\psi,\varphi;\mu_0) = \Psi(R,\psi,\varphi;-\mu_0)^* \quad (33)$$

Only in the absence of the potential ridge, i.e. for  $\mu_0 = 0$ , relation (29) reduces to the standard symmetry  $T\Psi = \Psi^*$  relation.

We think that the atomic process presented here occurs also in solids. A Gedanken experiment has shown how one Cooper pair can travel through a one-dimensional lattice.

## VI. OUTLOOK

Finally, we remark that the unusual observations presented here are not artefacts of 2-electron atoms. They must occur in all atoms and molecules because there exist potential ridges although in higher dimensions. For instance, for three highly excited electrons we expect Cooper triples with the geometry of a breathing equilateral triangle, one electron in each corner [11].

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