Wavefunctions and autoionisation of doubly excited states in
momentum space

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Abstract. We report results on the wavefunction representation of doubly excited states
of He and on their autoionisation probability amplitudes in momentum space. These are
presented in terms of conditional probability density and differential transition amplitude
plots. The correlated momentum wavefunctions are obtained by Fourier-transforming
position wavefunctions computed by multiconfigurational Hartree–Fock and variational
procedures. Special techniques are developed for the Fourier transform of the numerical
Hartree–Fock scattering orbitals. The differential transition amplitude plots lead to the
same conclusions regarding the mechanism of autoionisation as did our previous work in
position space.

1. Introduction

It is well known (Bethe and Salpeter 1957) that bound wavefunctions of atoms and
molecules can be obtained in the momentum representation (Dirac 1927, Jordan 1927).
The most common method used—and the one adopted in this work—involves Fourier
transformation of the position space wavefunctions (Podolsky and Pauling 1929, Hicks
1937, Coulson and Duncanson 1942, Duncanson and Coulson 1945, Rubinowitz 1948).
An alternative method, that of solving the momentum space integral Schrödinger
equation (Weyl 1928, Fock 1935, Levy 1950, Bethe and Salpeter 1957), is considered
less convenient for many-electron systems (McWeeny 1949) although it allows the use
of different definitions (Lombardi 1982).

A number of reasons, outlined below, have led us to the introduction of momentum
space into the study of autoionising doubly excited states (DES).

(i) Thus far, the theory and calculation of momentum space wavefunctions
(MOSWAF) of many-electron systems have dealt only with the ground state, examining
questions about shell structure, bonding, electron impact of Compton scattering, radial
and angular correlations, Coulomb holes, etc (see e.g. Duncanson and Coulson 1945,
information about highly excited states is completely lacking. Furthermore, since
electron correlation plays a crucial role for DES (contrary to many situations in the
(equilibrium) ground state where even orbital approximations are often quantitatively
useful), such states present a challenge in the construction of accurate MOSWAF.

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(ii) In the case of autoionising DES, the most relevant questions are related to their decay dynamics. For example, it is intriguing to know whether it is possible to relate wavefunction characteristics to autoionisation widths. In this respect, the depiction of dynamic processes (rather than static expectation values), like autoionisation or chemical reactions, in terms of the distribution of electronic momenta might provide a useful means of analysis. For example, the information contained in the diffuse highly excited and infinite range scattering state position space wavefunctions (POSWAF) is transformed into compact and localised descriptions. In particular, the Bessel function (a useful approximation for the study of autoionisation of negative ions, where the remaining atomic core has no charge) becomes a δ function of known energy.

(iii) The third reason is rather speculative and is related to group theory analysis of DES and to related appropriate basis sets. Fock’s (1935) solution for the H atom showed that the Podolsky-Pauling (1929) solutions are stereographic projections of hyperspherical harmonics onto the three-dimensional momentum hyperplane. The four-dimensional rotations in the projective momentum space constitute the symmetry group of the discrete spectrum of the Coulomb field, O(4), with the additional constant of motion being the Pauli-Lenz vector A (Pauli 1926, Bargmann 1937, Fock 1935). On the other hand, work in recent years on DES (Wulfman 1973, Sinanoğlu and Herrick 1975, Crance and Armstrong 1982, Herrick 1983) has shown a connection between approximations to the wavefunctions of DES and representations of O(4)×O(4), with Lie algebra generators being the operators B = l₁ + l₂ and A = A₁ - A₂. Thus, by analogy to the one-electron atom, it seems that accurate MOSWAF of DES might play a useful role as standard results for further research by group theory or geometry analysis.

2. Computational objectives

The goal of this work was to obtain accurate plots in momentum space of two quantities: the conditional probability density ρ defined as

\[ \rho(p_2, γ | p_1 = α) = \rho(p_1 = α, p_2, γ) \left( \int dp_1 \int dγ \rho(p_1 = α, p_2, γ) \right)^{-1} \]  \tag{1}

and the differential transition amplitude D defined as

\[ D(p_1, p_2, γ) = p_1^2 p_2^2 \Psi_0(p_1, p_2, γ)(H - E_0) U_{E_0}(p_1, p_2, γ) \]  \tag{2}

where α is fixed, γ is the angle between the two momenta, \( \Psi_0 \) is the initial-state square integrable MOSWAF, \( U_{E_0} \) is the final-state continuum MOSWAF and \( E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \).

The position space equivalents of equations (1) and (2) were introduced into the study of He DES by Rehms and Berry (1979, 1981). Earlier (Banyard and Taylor 1974, Beck and Nicolaides 1976), simplified calculations of ρ had been carried out on pair correlation functions. Recently, Komninos et al (1986) also studied the position space ρ and D for the He DES examined by Rehms and Berry (1979) and Ezra and Berry (1983). For ρ, our results coincide with theirs, though for D they differ substantially. Consequently, our proposal (Komninos et al 1986) for the mechanism of autoionisation of DES, which is based on the interpretation of D, disagrees strongly with their conclusions of the ‘generalised S₂ mechanism’ which is derived from the supposed dominance of the one-electron terms in the Hamiltonian. Our conclusion, instead, is that the contribution to autoionisation comes mainly from the interelectronic repulsion and the large overlap between bound and scattering orbitals in small regions of space.
Our choice of the quantities $\rho$ and $D$, defined by equations (1) and (2), thus has its origin in the background mentioned above. Apart from the practical interest in obtaining MOSWAF for bound and continuum states, we wished to see the 'pictures' which emerge in momentum space, possibly providing complementary means of understanding dynamic phenomena.

3. Theory and methods of computation

As was mentioned in the beginning, the MOSWAF of equations (1) and (2) were obtained by three-dimensional Fourier integration of the corresponding POSWAF, which are of high accuracy (Komninou et al. 1986). The theory and method for obtaining correlated POSWAF of DES have been given before (e.g., Nicolaides 1972, 1984, Nicolaides and Beck 1978, Komninou et al. 1983, Komninou and Nicolaides 1983, 1986). In their final form, these POSWAF, $\Psi_0$ and $U_{E_n}$, are expressed as linear combinations of symmetry-adapted configurations which contain optimised one-electron functions (orbitals) of the following three types: (a) Numerical bound orbitals constituting the zeroth-order multiconfigurational Hartree–Fock (MCHF) vector; (b) analytic, Slater-type orbitals (STO) representing the virtual function space; and (c) the scattering orbital of the free electron, which is obtained numerically by solving the frozen-core HF equations. The numerical orbitals are made orthogonal to lower core orbitals and are obtained by utilising modified versions of the computer codes of Froese Fischer (1978) and of Bates (1974).

The Fourier transformations are carried out numerically in the following way. Given the invariance of the spherical harmonics, it is straightforward to prove that the radial part $\phi(r)$ of an orbital transforms into $f(p)$ in momentum space, given by

$$f(p) = \sqrt{\frac{2}{\pi}} \frac{1}{L} \int_0^\infty r^2 \, dr \, \phi(r) j_L(pr)$$

where $j_L(pr)$ is the Bessel function. Note that equation (3) can only be integrated if $\phi(r)$ is square integrable. If the integration is performed numerically care must be given to the rapid oscillations of $j_L(pr)$ which start at moderate values of $p$. In order to account for this, we have adopted the method of Filon's quadrature (Hildebrand 1965).

As regards the Fourier transform of scattering functions, a different procedure was followed. The momentum representation for the pure-Coulomb wavefunction was studied long ago by Guth and Mullin (1951) and formal analytic expressions have been derived. The integral representation of the Green function of the Coulomb problem in momentum space has also been given by Schwinger (1964).

However, such expressions are not appropriate for direct numerical application. Besides that, the Coulomb partial wave does not constitute a good description of the electron scattered by an atomic or molecular ion in the interaction region. In a number of calculations on autoionisation widths (Nicolaides and Aspromallis 1983, Komninou et al. 1983, 1986, Komninou and Nicolaides 1983), the frozen-core HF solution has proven to be reliable, as was anticipated (Nicolaides 1972). Thus, in order to use Hartree-Fock continuum orbitals we had to implement general numerical procedures for the calculation of the Fourier transform of such orbitals. As mentioned above, equation (3) is not applicable since the integrand does not vanish at large $r$. The approach which we adopted is described below.
Consider the differential equation satisfied by \( \phi_k(r) \), the scattering orbital in position space:

\[
(-\frac{1}{2} \nabla^2 + V(r)) \phi_k(r) = \frac{1}{2} k^2 \phi_k(r).
\]

(4)

Upon taking the Fourier transform of both sides and making use of the plane-wave expansion formula and of the orthonormality of the spherical harmonics, we obtain

\[
f_k(p) = 2 \sqrt{\frac{2}{\pi}} \frac{1}{k^2 - p^2} \int_0^\infty r^2 \phi_k(r) V(r) j_p(r) \, dr \quad \text{for} \quad p \neq k.
\]

(5)

Equation (5) incorporates the characteristics of the potential from which the free electron is scattered. For example, if \( \phi_k \) is a Bessel function, its momentum space transform is readily seen to be a \( \delta \) function at \( p = k \). However, in the general case, evaluation of equation (5) is not as straightforward. We proceed as follows. For an ionic core, the tail of the potential is pure Coulombic, \( V^C(r) \), and \( \phi_k \) reduces to a phaseshifted Coulomb function \( \phi_k^C(r) \) for \( r > r_0 \). The integral may then be split into two integrals:

\[
\int_{a}^{\infty} r^2 \phi_k^C(r) V^C(r) j_p(pr) \, dr + \int_{0}^{r_0} r^2 j_p(pr)[\phi_k(r) V(r) - \phi_k^C(r) V^C(r)] \, dr.
\]

(6)

The first of these is known to be convergent and finite for all \( p \neq k \) (Landau and Lifshitz 1958). Thus, \( f_k \), as given by equation (5), is well defined at all non-singular points. The momentum space scattering function may then be computed from equation (5) at any value of \( p \neq k \) by numerical integration because the integrand involved drops off as \( r \) increases. Unfortunately, this damping is slow. Therefore, \( f_k \) was evaluated by a combination of Simpson's rule and asymptotic series expansion (Belling 1968). The Hartree–Fock momentum space scattering orbital outside the He\(^+\) Is core is shown in figure 1 (in au).

On the other hand, as \( p \to k \) the integral (5) does not converge, while \( k^2 - p^2 \) tends to zero. Expressions of this type have been examined by Altick (1969) in connection with the integral formulation of scattering theory. By analogy with his equation (21)

![Figure 1](image-url)
we have that, as \( p \to k \), \( f_2(p) \) oscillates rapidly as

\[
\text{Re}\{C(k)[(p-k)/2k]^{iz/k}\}
\]

(7)

where \( C(k) \) is a complex function of \( k \) (Aitick 1969) and fails to converge for \( p = k \) (branch point singularity). Thus, the singularity in equation (5) is a pole plus a branch point. Nevertheless, the momentum distribution may still be defined at \( p = k \) by introducing a factor \( e^{-\eta} \) for arbitrarily small values of \( \eta \), with the understanding that one will proceed to the limit of \( \eta \to 0 \) after having performed all the necessary integrations and when the singularity has been removed. The first integral then yields

\[
\int_0^{\infty} r^2 \phi^*_k(r) V(r) j_l(pr) \, dr
\]

\[
= \lim_{\eta \to 0} \left\{ \frac{2\Gamma^2(2l+2)}{[\eta^2 + (p + k)^2]^{l+1}} \text{Re} \left[ \frac{\Gamma[i(z/k - z'/p)]}{r(l+1+iz/k)\Gamma(l+1-iz'/p)} \right. \right.
\]

\[
\times \left( \frac{k-p+i\eta}{k+p+i\eta} \right)^{-l+1} \left( \frac{-k-p+i\eta}{k+p+i\eta} \right)^{iz/k}
\]

\[
\times F(l+1-iz/k, l+1+iz'/p; 1
\]

\[
+i(z/k - z'/p), [\eta^2 + (k-p)^2]/[\eta^2 + (k+p)^2] \right\}
\]

(8)

where \( F \) is the hypergeometric function and \( z' = 0 \).

The numerical techniques outlined above yield momentum space bound and free orbitals which are characterised by the following.

(1) The more diffuse the position space orbital is, the more compact the corresponding momentum orbital is. Localisation may offer conceptual or computational advantages, especially for highly excited states whose functions die out at very large distances. (For example, in the case of the \( 2s^1S \) \( \text{He} \), both the zeroth-order \( \text{MCHF} \) as well as the virtual orbitals are localised around \( p \sim 1-2 \) au.) When the scattering threshold is reached, the electron distribution is represented by a sharp peak of zero momentum.

(2) The momentum space radial functions become \( l \) dependent through the imaginary factor as well as through the Fourier integral (equations (3) and (5)).

4. Results

The conditional probability density distributions in momentum space in terms of the absolute values \( p_1 \) and \( p_2 \) of the two momentum vectors and the angle \( \gamma \) between them are shown in figures 2-3.

Due to differences in the relative distributions of the radial functions in terms of which \( p \) is computed, as well as due to the different signs with which the configurations mix in momentum space (arising from the \( l \)-dependent imaginary factors in the momentum space orbitals), the overall shape in momentum space does not, in general, resemble that of position space at all closely (Kommninos et al 1986). Important features characterising the state in position space are not necessarily retained here, and a rotor/antirotor classification (Ezra and Berry 1983, Kommninos et al 1986) (the term referring to the momentum vectors \( p_1, p_2 \)) does not seem feasible.
However, there are other features obtainable from these graphs which are useful indices for the study of autoionisation. One of these is the amplitude of the DES wavefunction at the momentum of the scattered electron. The resulting overlap readily gives a relative measure of the magnitude of the autoionisation rate.

Furthermore, closer analysis of the square-integrable wavefunctions in momentum space reveals information about the process of autoionisation which supports the mechanism suggested in our previous work in position space (Komninos et al 1986). Consider first the two lowest (2s$^2$ and 2p$^3$) S DES (figures 2(a), (b)), for which the scattered electron has momentum 1.5 au. The probability density for the 2s$^2$ state has
its maximum at $\gamma = 180^\circ$ if $p_1 = 1.5$. This means that the main contribution to the autoionisation amplitude occurs when the two electrons move in opposite directions, which confirms the interpretation of autoionisation as a collision process.

On the other hand, inspection of the momentum density distribution of the $2p^2$ state at $p_1 = 1.5$ shows a relatively small peak at $\gamma = 180^\circ$ and a larger peak around $\gamma = 0^\circ$. The smaller probability of the two electrons having opposite momenta at this value of $p_1$ is, according to the above, consistent with the much smaller autoionisation width of this state. Note that there are higher peaks of the probability density at 180$^\circ$ for smaller values of $p_1$, and the electrons do move in opposite directions with significant probability there, but none of them has the necessary kinetic energy to escape, i.e., the ‘collisions’ are inefficient.
Similar observations can be made for the $2s2p^1P^0$ and $3P^0$ pairs.

The non-smoothness of the momentum scattering orbital in the vicinity of the singularity at $k$ dictated the manner in which $D$ of equation (2) was evaluated. We took into account two facts. First, that the transformation of the integrand from position to momentum space can be done in a number of equivalent ways—all leaving the matrix element invariant. Second, that one such transformation allows the calculation of the integrand without any integration over the momentum scattering function. Therefore, in computing $D$ we have avoided the computation of a very accurate numerical momentum scattering orbital (in which case the infinite number of oscillations around $p = k$ would cause extreme practical difficulties).

Our solution to the problem of transforming the position space $D$ into the momentum space $D$ was the following. The kinetic and one-electron potential terms are

![Figure 4](image)

**Figure 4.** Differential transition amplitude in terms of the momentum variables $p_1$, $p_2$, $\gamma$ for the (a) $2s^2 \, 1S$ and (b) $2p^3 \, 1S$ states. The $\sin \gamma$ factor of the Jacobian is not included. The oscillations around $p_2 = 1.56$ au are due to the scattering function. The shape in the vicinity of the singularity (which should approach infinity) is truncated due to insufficient resolution.
straightforward to handle. The two-electron term was evaluated by subjecting each two-electron integral involving the scattering orbital \( \phi_k \) in position space to the transformation
\[
\frac{\langle \phi_k(r_1) \phi_k(r_2) | 1/r_{12} \phi_{\text{core}}(r_1) \phi_{\text{core}}(r_2) \rangle}{\langle \phi_k(p_1) V(p_2) | f_{\text{core}}(p_2 - p_1) U(p_2) \rangle}
\] (9)

where \( f_1 \) and \( f_{\text{core}} \) are the transformed \( \phi_1 \) and \( \phi_{\text{core}} \), and
\[
V(p_2) = -(2\pi)^{1/2} Z/2 \pi^2 p_2^2
\] (10)
\[
U(p_2) = (2\pi)^{-3/2} \int dr_2 \phi_2^* (r_2) f_2 (r_2) \exp(-i p_2 r_2). \] (11)

This transformation of the two-electron integral has (as opposed to other possible transformations) the advantage that the integral does not involve any integration over the illeveled momentum scattering function. Thus, the momentum scattering function appears only as a factor in the integrand of the one-electron terms.

Figure 4 presents \( D \) of equation (2) for the 2s\(^2\) and 2p\(^2\) \(^1\)S states of He.

One can see the singularities at \( p_2 = k \), the momentum of the free electron (truncated at some finite height as a result of insufficient resolution) and the rapid oscillations around these values of \( p_2 \). These arise from the one-electron terms and, when integrated out, are small. Apart from these features, one can observe the broad effect on the interelectron repulsion term, most significant at \( p_1 = 1.5, \gamma = 180^\circ \) in the 2s\(^2\) case and much smaller in the 2p\(^2\) case, for the reasons stated above. Notice that the two-electron term appears smooth in momentum space, as opposed to the \( 1/r_{12} \)-type singularity it exhibits in position space. This feature, along with the fact that in a fully orthogonal basis the one-electron terms make no contribution to the autoionisation width, may constitute an additional reason for the significance of the introduction of momentum space into the study of dynamical processes in highly excited states.

5. Synopsis

We have shown that it is possible to obtain information on autoionising states and the dynamics of the corresponding transition process in momentum space. This was done by taking the Fourier transforms of localised correlated wavefunctions and of numerical Hartree–Fock free orbitals. The method is general and applicable to a variety of highly excited states and transition processes in the continuous spectrum.

The first numerical application was carried out on the low-lying \(^1\)S and \(^1\l P\)\(^0\) doubly excited states of He, about which results have already been published from position space wavefunctions (Komninos et al 1986).

The analysis of the probability density distribution of the bound- and free-electron wavefunctions in momentum space indicates a large contribution to the autoionisation width from the region of momentum space where the two electrons move in opposite directions, one of them having the necessary kinetic energy to escape from the nuclear attraction. This observation is consistent with the relative decay rates of the states that were studied and supports the suggestion of a collision mechanism for the autoionisation process.

It is too early to judge the possible utility of momentum space in the study of DES. Nevertheless, the localisation in momentum space of highly excited or continuum orbitals and the smoothness of the integrand of the two-electron terms may offer
conceptual (and possibly computational) advantages and contribute, in general, towards the easy interpretation of the dynamics of decay.

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