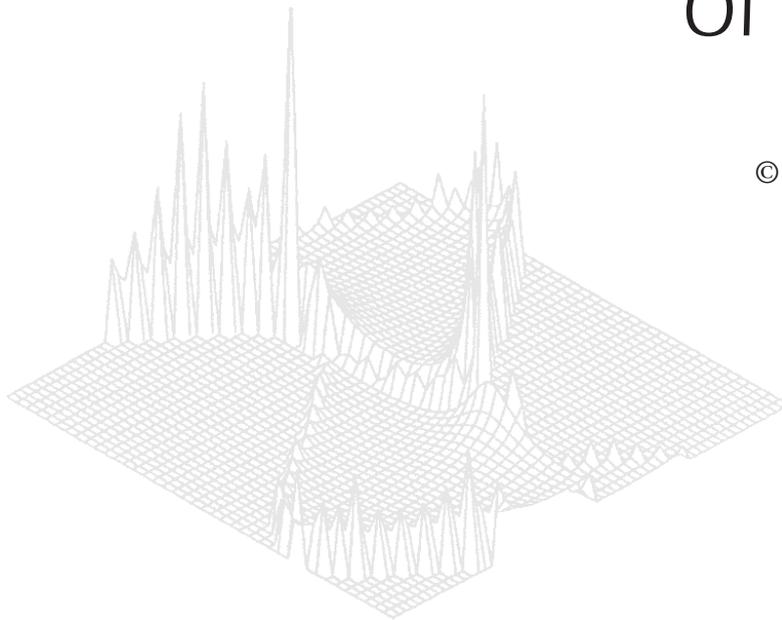

C S I R O P U B L I S H I N G

Australian Journal of Physics

Volume 52, 1999
© CSIRO Australia 1999



A journal for the publication of
original research in all branches of physics

www.publish.csiro.au/journals/ajp

All enquiries and manuscripts should be directed to

Australian Journal of Physics

CSIRO PUBLISHING

PO Box 1139 (150 Oxford St)

Collingwood

Vic. 3066

Australia

Telephone: 61 3 9662 7626

Facsimile: 61 3 9662 7611

Email: peter.robertson@publish.csiro.au



Published by **CSIRO PUBLISHING**
for CSIRO Australia and
the Australian Academy of Science



The Dynamics of Two-electron Atoms*

John S. Briggs

Fakultät für Physik, Universität Freiburg,
Hermann-Herder-Str. 3, D-79104 Freiburg, Germany.

Abstract

Since the first attempts to calculate the helium ground state in the early days of Bohr–Sommerfeld quantisation, two-electron atoms have posed a series of challenges to theoretical physics. Despite the seemingly simple problem of three charged particles with known interactions it took more than half a century after quantum mechanics was established to describe spectra of two-electron atoms satisfactorily. The evolution of the understanding of *correlated* two-electron dynamics and its importance for doubly excited resonance states is described in this overview.

1. Introduction

The theory of two-electron atoms has played an important role in the development of theoretical physics this century. The failure of the old quantum theory to describe a stable two-electron atom triggered the development of quantum mechanics. Once the basic formalism had been established by Heisenberg and Schrödinger early variational calculations produced remarkably good results for the ground state of helium and H^- and broke the ground for the general acceptance of quantum mechanics.

In Section 2 we will briefly sketch the attempts of the old quantum theory to describe the helium ground state. In particular, a forgotten idea by Heisenberg comes surprisingly close to recent findings of classical dynamics which turns out to be relevant for high lying resonances of helium. Following the first synchrotron absorption experiments detecting doubly-excited states in the early sixties, it became clear that the effective single particle picture, familiar from the successful Hartree–Fock approximation, was inadequate to understand two-electron resonances. As a consequence, sophisticated alternative quantum approximations were developed over the next thirty years. The most important concepts were a group theoretical approach and two adiabatic approximations. These concepts successfully explained the high degree of regularity in the spectra of two-electron resonances, i.e. features which could not be accounted for by an effective single particle picture. Rather, they are intrinsically related to the *correlated* dynamics of two electrons. In Section 3 the results achieved by the approximate quantum

* Refereed paper based on a contribution to the Australian–Germany Workshop on Electron Correlations held in Fremantle, Western Australia, on 1–6 October 1998.

methods, in particular the existence of approximate collective quantum numbers and propensity rules for the decay of resonances, are summarised.

Over the last decade the regime of extremely high excitation, i.e. principal quantum numbers N, n for both electrons of $N \approx n \geq 10$, has become accessible, both experimentally and computationally. For these high excitations the approximate quantum numbers begin to lose their meaning and the regularities in the two-electron resonance spectrum start to dissolve. Moreover, even if applicable, the spectroscopic concept of isolated resonances identified by a set of quantum numbers becomes very questionable if the density of resonances per unit energy tends to infinity, which is the case towards the three-body break-up limit $E = 0$ when $N \approx n \rightarrow \infty$. Hence, one needs a new concept to understand two-electron dynamics in this regime of extreme double-excitation. The concept is provided by a modern semiclassical approach. Its development over the last few years has led to impressive progress in the quantitative description of the resonances. The backbone of these semiclassical descriptions are the periodic orbits of the full classical two-electron system without approximations. Surprisingly, from the shortest and simplest periodic orbits and from their stability properties one can draw a picture of two-electron excitation dynamics which agrees extremely well with the results of the quantum approximations explaining the regular spectrum of intermediate double excitation. However, the periodic orbits have one advantage that goes beyond the simple structural picture: A representation of the spectra in terms of periodic orbits does not rely on an explicit quantisation scheme based on the quasi-separability of the problem in (collective) coordinates or the existence of approximate quantum numbers. This advantage might point the way into the extreme excitation regime where the increase in the number of resonances renders a description in terms of quantum numbers meaningless. One tool which has already proved to be very useful to characterise dynamical features in the extreme excitation limit for hydrogen in the magnetic field is scaled periodic orbit spectroscopy. As we will discuss in Section 4 an incredibly complex energy spectrum with many (overlapping) resonances can look quite ordered, if properly Fourier transformed into the time domain where peaks at certain times indicate the periods of relevant periodic orbits.

We will deal exclusively with the nonrelativistic two-electron Hamiltonian in atomic units,

$$H = \frac{\vec{p}_1^2 + \vec{p}_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (1)$$

where Z is the nuclear charge, r_k ($k = 1, 2$) denote the electron–nucleus distances and the distance between the electrons is r_{12} . We will discuss both helium and H^- .

2. Pre-quantum Attempts to Quantise Helium and Heisenberg’s Forgotten Idea

In 1913 Bohr succeeded in explaining the energy levels of the hydrogen atom in terms of a quantisation of the classical Kepler orbits. Numerous attempts to explain the ground state of helium by quantising different two-electron periodic orbits in a

similar manner failed.¹ All these attempts were based on the belief that (i) the ground state of helium is related to a single periodic orbit of the electron pair, (ii) the electrons move on symmetric orbits with $r_1 = r_2$ for all times, (iii) orbits where the electrons hit the nucleus ('Pendelbahnen', see Born 1925) are excluded and (iv) the quantum number n in the quantisation condition is an integer.

Heisenberg's interest in the helium problem was stimulated by Bohr in 1922. Sommerfeld and Heisenberg devised as a possible classical ground state configuration a model where the electrons move *asymmetrically* on two different Kepler ellipses of the same shape but oriented in opposite directions, sketched by Heisenberg in a letter to Sommerfeld (Heisenberg 1922) (see Fig. 1). Heisenberg outlined in the letter a calculation of the ground state energy based on this electron-pair motion. As an important achievement from today's point of view, he introduced a second quantisation condition, $\oint p_\varphi d\varphi = n_\varphi h$, for the motion of the angle φ between the major axes of the two orbits under the influence of the mutual electron interaction (see Fig. 1). Moreover, he allowed for n_φ to be *half-integer*. Including the electron repulsion in a perturbative manner, Heisenberg arrived at an ionisation potential of 24.6 V, compared to the best experimental value of 24.5 V at that time! Discouraged by Bohr and Pauli who harshly criticised the concept of non-integer quantum numbers, Heisenberg never published his calculation, although it was referred to by Sommerfeld (1923).

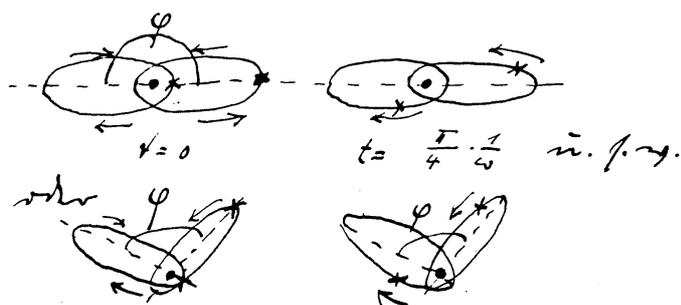


Fig. 1. Sketch of the periodic electron pair motion proposed by Heisenberg in a letter to Sommerfeld in 1922 as a candidate for a classical ground state configuration of helium.

In the meantime it has become clear that Heisenberg's success was accidental (Solov'ev 1985; Tanner *et al.* 1998). Consequently, attempts to describe (Born and Heisenberg 1923) excited states of helium in a similar fashion failed. The pessimistic mood in the early twenties concerning the treatment of two-electron atoms becomes apparent in a conclusion given by van Vleck (1922): 'The conventional quantum theory of atomic structure does not appear to be able to account for the properties of even such a simple element as helium, and to escape from this dilemma some radical modification in the ordinary conceptions of the quantum theory or of the electron may be necessary.'

History has shown that van Vleck was right. Quantum mechanics as we know it today took off quickly once the concepts developed by Schrödinger and Heisenberg had been proven to work, e.g. for the helium ground state which

¹A summary can be found in Leopold and Percival (1980).

Hylleraas (1929) was able to calculate accurately using variational techniques. The singly excited states of two electron atoms were also relatively simple to understand and with the mean field theory, i.e. the Hartree–Fock approach, the structure of almost the entire periodic table could be explained.

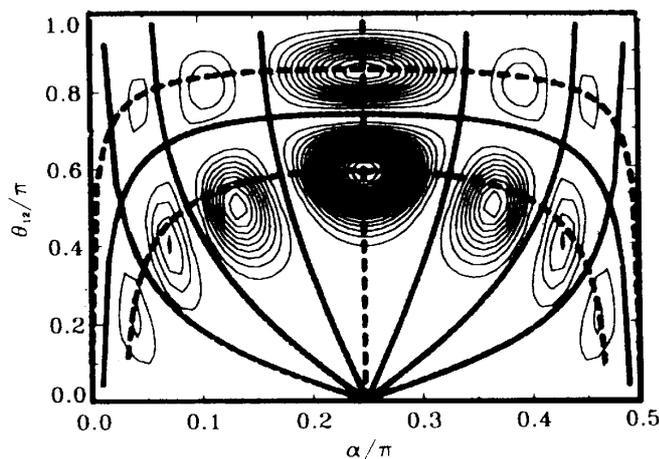


Fig. 2. Two-electron density at $(r_1^2 + r_2^2)^{\frac{1}{2}} = 80$ a.u. for a resonant state with $1P^o$ symmetry of H^- from an adiabatic hyperspherical calculation (Sadeghpour and Greene 1990). The coordinates are $\theta_{12} = \angle(\vec{r}_1, \vec{r}_2)$ and $\tan \alpha = r_1/r_2$. Overlaid are the spheroidal nodal lines $\lambda = (r_1 + r_2)/r_{12}$ and $\mu = (r_1 - r_2)/r_{12}$ predicted by the adiabatic molecular approximation (Rost *et al.* 1990).

3. Quantum Approximations for Double Rydberg Atoms

New surprises came with the first experiment on *doubly*-excited states of two-electron atoms by Madden and Codling (1963). The observed resonance spectrum looked quite different from what had been expected from a Hartree–Fock picture: Only two instead of three Rydberg series were observed below the second ionisation threshold of helium, $N = 2$. Moreover one series was very weak, and none of the energies of the resonances agreed with the mean field predictions. This was correctly interpreted as a signature of strong electron–electron correlation—and the tools to understand it have been developed over the last 30 years. The adiabatic hyperspherical, molecular and a group theoretical approximation (for reviews see Herrick 1983; Lin 1986; Rost and Briggs 1991) have mainly shaped today’s understanding of moderately excited double Rydberg atoms in terms of approximate quantum numbers and propensity rules for the decay and radiative transitions (dipole matrix elements) of the resonances. These properties come from a well-defined nodal structure of resonant wavefunctions near the maximum probability density exemplified in Fig. 2. These results are in remarkable agreement with the latest photoabsorption experiments—for a review see Rost *et al.* (1997).

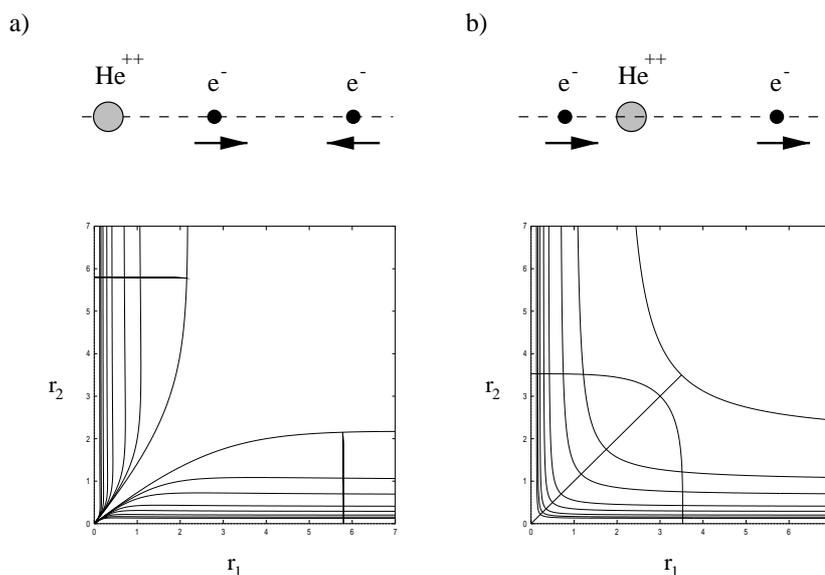


Fig. 3. The helium potential $V(r_1, r_2) = -Z/r_1 - Z/r_2 + 1/|r_1 \pm r_2|$ in the classically allowed regime $V \leq E$ together with the shortest periodic orbits: (a) the Zee configuration with both electrons on one side of the nucleus together with the stable frozen planet orbit (FP) and (b) the eZe configuration with electrons on different sides of the nucleus together with the unstable asymmetric stretch orbit (AS) and the symmetric stretch orbit ($r_1 = r_2$).

4. Semiclassical Dynamics of Double Rydberg Atoms

In contrast to the semiclassical methods of the old quantum theory discussed in Section 2, contemporary semiclassical theory has a sound mathematical foundation (Gutzwiller 1990). Based on this background it is indeed possible to understand the spectrum of double Rydberg atoms in terms of a few, more exactly three, periodic orbits only. This is very much in the spirit of the old quantum theory. However, the three orbits are not guessed or arbitrarily picked, rather they represent the first order approximation in a well-defined expansion of the semiclassical Green function in terms of periodic orbits (PO).

(4a) Three Fundamental Periodic Orbits and Their Role in Two-electron Dynamics

In Fig. 3 the three fundamental periodic two-electron orbits, which are all collinear, are sketched. The *frozen planet* orbit (Fig. 3a) has the two electrons on the same side of the nucleus. This orbit is classically stable and obtained its name from the fact that the outer electron moves very little and represents almost a ‘frozen planet’. The *asymmetric stretch* orbit has the two electrons on opposite sides of the nucleus. The orbit is slightly unstable and exhibits an asymmetry in the electron distances, i.e. $r_1(t) \neq r_2(t)$. This is in contrast to the third orbit, the so called *symmetric stretch* or Wannier orbit with $r_1(t) = r_2(t)$, also drawn in Fig. 3b.

(4b) Scaling and Rydberg Formulae

If a periodic orbit (PO) of a system with pure Coulomb forces is quantised it produces automatically a Rydberg series. The reason lies in the scaling

property of the classical Hamiltonian which can be made energy independent in scaled coordinates $\vec{p}_i^s = \vec{p}_i(-E)^{-1/2}$ and $\vec{r}_i^s = \vec{r}_i(-E)$. This leads to the scaled action $S_s = S(-E)^{1/2}$. Hence, quantisation of the (unscaled) action produces a Rydberg series of the form $E_n = -(S_c/2\pi)^2/(n-\mu)^2$, where the semiclassical quantum defect μ consists of the stability properties of the quantised PO, i.e. the characteristics of the dynamics in phase space orthogonal to the PO.

The *frozen planet* orbit is stable. Hence, one can apply torus quantisation according to the Einstein–Brillouin–Keller (EBK)—leading to a Rydberg formula (Richter *et al.* 1992),

$$E_{m,k,\bar{n}} = -\frac{(S_{\text{FP}}/2\pi)^2}{[(m + \frac{1}{2}) + 2(k + \frac{1}{2})\sigma_1 + (\bar{n} + \frac{1}{2})\sigma_2]^2}, \quad m, k, \bar{n} = 0, 1, 2, \dots \quad (2)$$

For helium the scaled action of the orbit is $S_{\text{FP}}/2\pi = 1.4915$ and $\sigma_1 = 0.4616$, $\sigma_2 = 0.0677$ are the winding numbers for the dynamics in the degree of freedom perpendicular to the collinear subspace and for the dynamics in the collinear plane of the PO respectively. The quantum number m corresponds to nodes along the PO, and k and \bar{n} to nodes in the degrees of freedom perpendicular to the PO.

The asymmetric stretch orbit on the other hand is unstable. Quantisation of this orbit alone is in the strict sense not appropriate and may be viewed as a first order truncation of a series expansion of the semiclassical Green function in terms of POs (Ezra *et al.* 1991; see also Tanner and Wintgen 1995 and Tanner *et al.* 1999),

$$E_{m,k} = -\frac{(S_{\text{AS}}/2\pi)^2}{[m + \frac{1}{2} + 2(k + \frac{1}{2})\sigma_{\text{AS}}]^2}, \quad m, k = 0, 1, 2, \dots \quad (3)$$

For helium we have $S_{\text{AS}}/2\pi = 1.8290$ and $\sigma_{\text{AS}} = 0.5393$ is the winding number for the dynamics in the bending degree of freedom. The quantum numbers m and k describe excitation along and perpendicular to the orbit which in turn corresponds to intra-shell excitation and vibrational excitation in the bending degree of freedom, respectively.

The energies of resonances characterised by excitation along these two orbits follow very closely the single orbit quantisation from equations (2) and (3) as can be seen in Fig. 4. The symmetric stretch PO (Fig. 3*b*) is highly unstable (Richter and Wintgen 1990) and incapable of supporting quantum resonances. However, this PO is the main decay path for resonances in two-electron systems. It can be easily reached by the asymmetric stretch type resonances, but not by the frozen planet ones. Hence, the latter ones have much longer lifetimes on average.

In summary, the three simplest periodic orbits give an excellent qualitative and semi-quantitative understanding of the double-Rydberg dynamics for moderate excitation.

(4*c*) Scaled Periodic Orbit Spectroscopy

When infinitely many, partially overlapping resonances occur in the spectrum as the double ionisation threshold is approached, a description of the spectrum

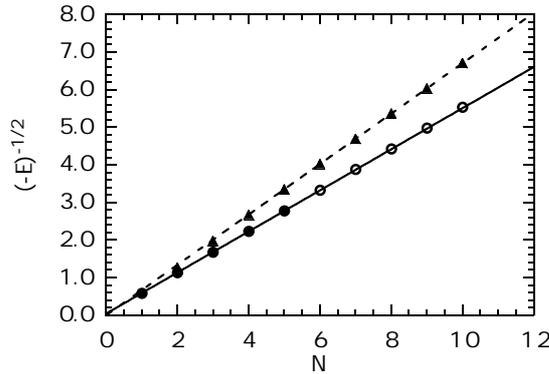


Fig. 4. Energies of quantum resonances of asymmetric stretch (circles) and frozen planet (triangles) character. The lines are the semiclassical energies predicted from equation (3) (solid) and equation (2) (dashed) respectively. Open circles indicate states which are not observable in the experiment due to strong interaction with an entire Rydberg series. In the quantum simulation they can be calculated by discarding the Hilbert space representing the Rydberg series—see Bürgers *et al.* (1995).

in terms of these resonances becomes meaningless. The previous paragraph gives already a hint of an alternative: Each of the periodic orbits gives rise to an infinite series of resonances. Hence, the question arises if there is a way to describe the spectrum directly in terms of the properties (stability and length, i.e. period or action) of the periodic orbits. This is indeed the case and the tool which has been developed is scaled periodic orbit spectroscopy (Friedrich and Wintgen 1989). It makes heavy use of the classical scaling property of the Hamiltonian, in particular that the action $S_j(E)$ of the periodic orbit j can be written as $S_j(E) = S_j(E = -1)|E|^{-1/2} \equiv s_j z$. In a conventional way we can express the density of resonant states with position E_n and widths Γ_n as

$$d(E) = \frac{1}{\pi} \sum_n \frac{\Gamma_n/2}{(E - E_n)^2 - (\Gamma_n/2)^2}.$$

As a function of $z = |E|^{-1/2}$ instead of E we can define the Fourier transform with respect to the scaled action space s , $f(s) = \int dz e^{-isz} d(z)$. This finally transforms the density of states $d(E)$ into the power spectrum of the periodic orbits, where a peak appears at each action s which corresponds to a periodic orbit (Qiu *et al.* 1996),

$$F(s) = |f(s)|^2 \approx \sum_{jk} |a_{jk}|^2 \delta(s_{jk} - s). \quad (4)$$

An actual action s_{jk} belongs to the k th repetition of the j th periodic orbit. For helium resonances the impressive simplification of the spectrum going from the

energy to the action domain is demonstrated by Qiu *et al.* (1996) and by Grémaud and Gaspard (1998). This relatively new tool can be used either to construct semiclassical spectra directly from periodic orbits, or to interpret experimentally or numerically obtained quantum spectra by merely Fourier transforming them after proper scaling.

5. Summary and Outlook

We have given a very brief overview of the research on double Rydberg atoms, covering the time since 1920. The astonishing order in the non-separable two-electron dynamics for moderate double-excitation energies is well understood in terms of quasi-separable approximations leading to approximate quantum numbers and propensity rules for autoionisation and radiative transitions. The agreement of theoretical predictions with recent high resolution experiments is very good (Rost *et al.* 1997).

In the extreme excitation regime ($N \approx n \geq 10$) the order in the resonance spectrum begins to dissolve (Bürgers *et al.* 1995) and the increasing density of resonances calls for new concepts to describe two-electron spectra in this energy regime. Periodic orbit spectroscopy provides such a tool. In the future, enhanced experimental as well as numerical capabilities will permit the study of the limit of double excitation, i.e. $E \rightarrow 0$, towards the double ionisation threshold. This limit is a very interesting singular point in the two-electron spectrum and connects extreme excitation ($E < 0$) with threshold double-ionisation ($E > 0$) (Rost and Tanner 1997).

Acknowledgments

It is a pleasure to acknowledge the active help of Jan Michael Rost in the preparation of this manuscript; a result of many years of fruitful collaboration on two electron atoms. Financial support from the Deutsche Forschungsgemeinschaft (SFB 276 in Freiburg) is also gratefully acknowledged.

References

- Born, M. (1925). 'Vorlesungen über Atommechanik' (Springer: Berlin) [English trans. 'The Mechanics of the Atom' (Ungar: New York, 1927)].
- Born, M., and Heisenberg, H. (1923). *Z. Phys.* **16**, 229.
- Bürgers, A., Wintgen, D., and Rost, J. M. (1995). *J. Phys. B* **28**, 3163.
- Ezra, G. S., Richter, K., Tanner, G., and Wintgen, D. (1991). *J. Phys. B* **24**, L413.
- Friedrich, H., and Wintgen, D. (1989). *Phys. Rep.* **183**, 37.
- Grémaud, B., and Gaspard, P. (1998). *J. Phys. B* **31**, 1671.
- Gutzwiller, M. (1990). 'Chaos in Classical and Quantum Mechanics' (Springer: Berlin).
- Heisenberg, W. (1922). Archive of the Deutsches Museum, Munich.
- Herrick, D. R. (1983). *Adv. Chem. Phys.* **52**, 1.
- Hylleraas, E. A. (1929). *Z. Phys.* **54**, 347.
- Leopold, J. G., and Percival, I. C. (1980). *J. Phys. B* **13**, 1037.
- Lin, C. D. (1986). *Adv. At. Mol. Phys.* **22**, 77.
- Madden, R. P., and Codling, K. (1963). *Phys. Rev. Lett.* **10**, 516.
- Qiu, Y., Müller, J., and Burgdörfer, J. (1996). *Phys. Rev. A* **54**, 1922.
- Richter, K., and Wintgen, D. (1990). *J. Phys. B* **23**, L197.
- Richter, K., Briggs, J. S., Wintgen, D., and Solov'ev, E. A. (1992). *J. Phys. B* **25**, 3929.
- Rost, J. M., and Briggs, J. S. (1991). *J. Phys. B* **24**, 4293.
- Rost, J. M., and Tanner, G. (1997). In 'Classical, Semiclassical and Quantum Dynamics in Atoms', Lecture Notes in Physics 485 (Eds H. Friedrich and B. Eckhardt), p. 274 (Springer: Berlin).

- Rost, J. M., Schulz, K., Domke, M., and Kaindl, G. (1997). *J. Phys. B* **30**, 4663.
- Sadeghpour, H. R., and Greene, C. H. (1990). *Phys. Rev. Lett.* **65**, 313.
- Solov'ev, E. A. (1985). *Sov. Phys. JETP* **62**, 1148.
- Sommerfeld, A. (1923). *J. Opt. Soc. Am.* **7**, 509.
- Tanner, G., and Wintgen, D. (1995). *Phys. Rev. Lett.* **75**, 2928.
- Tanner, G., Richter, K., and Rost, J. M. (1999). *Rev. Mod. Phys.*, to be published.
- van Vleck, J. H. (1922). *Philos. Mag.* **44**, 842.

Manuscript received 21 December 1998, accepted 30 March 1999