# Anisotropy Parameters and Adiabatic Approximations for Two-electron Atoms and Ions\*

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# Abstract

In dynamial processes atomic systems evolve from a condensation region at small distances where all particles are close together to an asymptotic region where some of the constituent particles are free and accessible to measurement. This dynamical evolution is characterised by the Jost matrix. Evaluation of the Jost matrix generally involves complex calculations, but considerable simplification is achieved when the evolution can be described in terms of adiabatic or diabatic potential curves. For low energy ion-atom and atom-atom collisions standard molecular potential curves have long been used. For low energy electron-atom scattering and photo-ionisation similar molecular-like potential curves have been proposed. There is no *a priori* justification for the adiabatic approach in these latter systems, thus confrontation with experiment is crucial for further development of this theory. Anisotropy parameters represent a particularly appropriate probe of the various adiabatic representations. This is illustrated by studies of photo-ionisation of helium at the n = 2 threshold. Potential curve crossings are important here and their relevance to the anisotropy parameters is illustrated.

# 1. Introduction

The scattering of electrons from atomic and molecular systems is conventionally characterised by the scattering matrix with elements  $S_{ii}$  and associated wave functions which incorporate incoming and outgoing waves representing the motion of a single electron. The indices *i* and *j* here refer to channels defined when the incident electron is far from the atom or ion with which it interacts. Fano (1987) has emphasised that an alternative picture in terms of the Jost matrices  $J^+$  and  $J^-$  with elements  $J^+_{\beta i}$  and  $J^-_{i\alpha}$  respectively offers conceputal advantages relative to the S-matrix approach. Here the index i represents the asymptotic channels as before, but  $\alpha$  represents a new channel called a condensation channel since it relates to the behaviour of the system when the incident electron is close to the atomic core. The superscripts - and + refer to outgoing and incoming waves so that  $J_{i\alpha}$  describes the connection between an incoming wave in a superposition of asymptotic channels *i*, *j*, ... evolving into a superposition of condensation channels  $\alpha$ ,  $\beta$ , ... at small distances. This is illustrated in the top part of Fig. 1. Here the condensation region is confined within a radius *a* and the propagation from

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**Fig. 1.** Schematic illustration of a spherical wave evolving from the asymptotic region towards a condensation region represented by  $J_{i\beta}^-$  (upper figure). The lower figure illustrates the outward motion represented by  $J_{\alpha i}^+$ .

asymptotic to condensation region is described in terms of the coordinate r, which will be referred to here as the reaction coordinate. This coordinate can be any coordinate that measures the overall size of the system so that r = 0 corresponds to the condensation region and  $r \rightarrow \infty$  to fragmentation. In the lower portion of the figure the complimentary evolution from the condensation region outwards as parametrised by the matrix  $J^+_{\alpha i}$  is illustrated. The *S*-matrix is the product of the  $J^+$  and the inverse of  $J^-$ ;

$$S_{ij} = \{J^+[1/J^-]\}_{ij} = \sum_{\alpha} J^+_{i\alpha} [1/J^-]_{\alpha i} \,. \tag{1}$$

Because the condensation channel indices  $\alpha$  in equation (1) are summed over, the only formal requirement that the set of condensation channels must satisfy is completeness. This is a very general requirement and allows considerable freedom in choosing them. With a judicious choice of condensation channels the sum in equation (1) could be truncated after a few terms. If the propagation from condensation region to asymptotic region is adiabatic and the reaction coordinate r is an adiabatic variable, then only one term suffices and the system evolves from a single such condensation channel to a particular linear combination of energy-degenerate asymptotic channels. Because the energy is minimised at each value of r in an adiabatic picture, the system must evolve into a superposition of asymptotic channels *i, j,...* which are degenerate in energy. Such degenerate channels generally describe the geometric properties of the asymptotic channels and thus they are best probed by observations of anisotropy parameters which examine the shape and circulation properties of atomic charge clouds. In the special case of hydrogenic ions and atoms there is an additional degeneracy which can be probed by measurements of the extended set of anisotropy parameters of Burgdörfer (1983). A special case of one of these parameters, namely, the 2p/2s excitation ratio will be employed later.

#### 2. Application to the Photo-ionisation of He

To apply these ideas, it is necessary to select the condensation channels, the reaction coordinate, and the asymptotic channels. This is most reliably carried out in a specific physical context. As a specific physical system, consider a two-electron ion or an electron colliding with a single electron ion or atom. In either event, we deal with the states of a two-electron system. For definiteness, consider also the photo-ionisation of the system so that an outgoing electron is produced. Thus we consider

$$h\nu + \text{He} \rightarrow \text{He}^+ + \text{e}^-$$
 (2)

or

$$h\nu + H^- \rightarrow H + e^-$$
 (3)

where  $h\nu$  represent a photon and the He<sup>+</sup> ion or H atom in the final state may be excited. Some choices of the condensation states that have been discussed in the literature are the doubly excited symmetry basis (DESB) of Herrick (1975) the molecular-like states of Feagin and Briggs (1986), and the hyperspherical adiabatic states of Macek (1968).

The normal hydrogenic independent particle orbitals for two electrons are labelled by  $n_i l_i m_i$  where i = 1, 2 in the approximation that the spin-orbit interaction is neglected, in the first approximation. Since total angular momentum is a good quantum number, states of fixed total orbital angular momentum labelled by  $n_1n_2LM$  are formed. If both  $n_1$  and  $n_1$  are greater than unity, these independent particle states are energy-degenerate and it is necessary to form linear combinations of such states to obtain a good first-order set of states. This combination is normally found by diagonalising the electron-electron interaction  $1/r_{12}$ . Since this cannot be done generally, Herrick (1975) chose a set of basis states that diagonalised a different operator, namely  $O_{12} = \frac{3}{2}(r_1^2 + r_2^2) - 2r_1 \cdot r_2$ . Since this operator involves  $r_1 \cdot r_2$  it represents the electron-electron correlation in some approximation. It is found that for the most important doubly excited states, this DESB representation is indeed an improvement over the single particle orbitals. These DESB states are labelled by the quantum numbers  $\{n_1n_2LM,K,T\}^A$ , where K and T are new quantum numbers appropriate to the linear combination of states that diagonalises  $O_{12}$ . The quantum number A introduced by Lin (1984) takes on the values {+,-,0} and is convenient to further characterise the states. Channel labels are obtained by omitting the principal quantum number of one electron, say  $n_2$  (corresponding to  $n_2 \rightarrow \infty$ ). The remaining principal quantum number then refers to the final state of the ion in the reaction (2). Thus we consider channel DESB labels  $\{nLM, K, T\}^A$ .

The molecular-like (MO) condensation channels of Feagin and Briggs (1986) employ eigenstates of the system with the electron-electron vector  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ held fixed in first approximation. The quantum numbers appropriate in this case are the projection of the two-electron angular momentum on the  $r_{12}$ axis, called m, the angular momentum L, the projection M of the total angular momentum on a space-fixed axis, and the projection T of the total angular momentum on  $r_{12}$ . The channels are further identified by the state of the ion when one of the electrons moves to infinite distance. This introduces a principal quantum number *n* and a parabolic quantum number  $n_{\xi}$ . This latter quantum number relates to the K quantum number of Herrick according to  $K = n - T - 1 - 2n_{\xi}$  and thus the DESB labels may be used for the MO channels also. One of the principal virtues of the MO description is that it allows one to interpret the DESB states in terms of adiabatic potential curves and eigenstates. This is needed in order to connect the condensation channels with the asymptotic channels. It also provides a link with the third set of states, namely, the adiabatic hyperspherical channels of Macek (1968).

The hyperspherical adiabatic states are obtained by solving the two-electron Schrödinger equation in an approximation where the hyper-radius  $R = (r_1^2 + r_2^2)^{\frac{1}{2}}$ is held fixed, in the first approximation. This gives a set of condensation channels (for a given spin *S*) which are labelled by *LM* and a new index  $\mu$ which simply labels the order of the adiabatic potential curves. The index  $\mu$ gives little information on the nature of the states so it is appropriate to adapt the DESB labels for the channels. This connection is made possible by Feagin and Briggs' MO potential curves which show a surprisingly close similarity with the hyperspherical adiabatic potential curves. Thus for all three of the condensation channels we employ the labels {*nLM*,*K*,*T*}<sup>*A*</sup> recognising that the basis states in the three representations differ.

Our second step is to identify the appropriate reaction coordinate r. In the case of the MO and hyperspherical representations the choices are clear; r represents  $r_{12}$  in the MO picture and R in hyperspherical picture. A reaction coordinate in the DESB representation is not clearly identified, since the classification is not based on an adiabatic approximation. Here we will employ the MO connection between condensation and asymptotic channels for the DESB representation, since, as shown by Feagin and Briggs (1986), the DESB quantum numbers have a simple physical interpretation in the MO picture.

The third step is to identify the asymptotic channels i, j, ... It is often best to regard these as set by the apparatus that observes the final state. Since one usually observes specific energy eigenstates, the principal quantum number n is appropriate. By observing radiation emitted in the decay of a final state, one can also determine the orbital angular momentum quantum number l. In the simplest case we distinguish between 2s and 2p states by the Lyman-alpha emission of the 2p state and the electric field quenching of the 2s state. Additional parameters are obtained by observations of alignment and orientation. Here we will identify asymptotic channels somewhat differently. We still employ the *n* label but recognise that the field of the outgoing electron mixes degenerate Stark states of the excited ion. This mixing implies that the asymptotic states diagonalise the projection of the electric field of the outgoing electron  $-\mathbf{r}_2/r_2^3$  onto the coordinate  $\mathbf{r}_1$  of the electron remaining with the ion. That is, one diagonalises  $\mathbf{r}_1 \cdot \hat{\mathbf{r}}_2/r_2^2$ . It turns out that the DESB channels and the MO states at large distances become identical to these particular configuration mixed states. The hyperspherical adiabatic states at large distances diagonalise the sum of the electric field term and a new term  $l_2^2/2r_2^2$ , representing effects of the angular momentum of the outgoing electron. There is also an additional term  $\frac{1}{3}l_1^2$  which has no physical significance. Its effect is generally small, so it will be neglected in the



**Fig. 2.** Adiabatic potential curves of He computed in the molecular orbital (upper figure) and the hyperspherical representations (lower figure).

remainder of this discussion. The asymptotic channels in the hyperspherical approximation then diagonalise the 'dipole' operator

$$D_{12} = l_2^2 + 2\mathbf{r}_2 \cdot \hat{\mathbf{r}}_1 \,. \tag{4}$$

Herrick (1978) showed that within the degenerate set of basis states nlm the operator  $\mathbf{r}_{12} \cdot \mathbf{L}$  commutes with  $D_{12}$  and that the eigenvalues of this operator are identical to the quantum number K in the approximation that  $l_1^2$  in equation (3) is neglected.



**Fig. 3.** The 2p/2s ratio computed in the molecular orbital representation and the hyperspherical adiabatic approximation compared with the experimental data of Woodruff and Samson (1982). The solid curve assumes only the dominant '+' channel is populated. The dashed curves give the limits obtained with a 1.7% admixture of the '-' channel (see Starace and Macek 1987).

Adiabatic potential curves connecting to the n = 2 states of He<sup>+</sup> calculated in the hyperspherical approximation and in the MO representation are shown in Fig. 2. Note the qualitative similarity of the <sup>1</sup>P<sup>0</sup> curves which are relevant for photo-ionisation. According to the Franck-Condon principle one expects the curve which is lowest at small R to be most strongly excited at low outgoing electron energy. This curve connects with the  $\{K,T\}^A = \{0,1\}^+$  state  $(2p\pi_u)$  in the MO representation) at large distances. The 2p/2s cross section ratio predicted in the DESB and MO representations is infinite since the  $\{0,1\}^+$ channel has no 2s component in these approximations. Alternatively, the hyperspherical approximation requires diagonalisation of the operator  $D_{12}$  and the corresponding eigenstate does have a 2s component so that the ratio is predicted to be finite. Exact diagonalisation of  $D_{12}$  gives a  $\{0,1\}^+$  with a 2s component such that the 2p/2s cross section ratio is 1.5. Fig. 3 compares this ratio with the experimental data of Woodruff and Samson (1982). The



**Fig. 4.** Hyperspherical adiabatic potential curves connecting to the n = 3, 4 states of He<sup>+</sup> showing the narrow avoided crossing between the lowest two curves.



**Fig. 5.** Asymmetry parameter  $\beta(n)$  for the lowest energy electrons at successive thresholds. The solid curve is the theoretical result of Greene (1980) using the hyperspherical adiabatic representation. The molecular orbital and DESB representations gives a constant  $\beta = -1$ . The experimental points are from Heimann *et al.* (1986).

agreement is moderate. We know that the channel  $\{1,0\}^ (3p\sigma_u)$  in the MO representation) is populated in an amount of  $1 \cdot 7\%$ . When this admixture is introduced it can add or subtract from the dominant component depending upon the phase of the photo-ionisation matrix elements. This then gives the limits indicated by the dotted lines in Fig. 3. Since these limits encompass the data we see that a correct prediction of the ratio requires using eigenstates

which diagonalise the operator in equation (2) and a small admixture of channels other than the dominant one.

The asymmetry parameter  $\beta$  which determines the angular distribution of the photoelectrons according to

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos\theta)] \tag{5}$$

is determined by the asymptotic admixture of m = 0 and m = 1 states in the final channel. In the MO and DESB representations only the  $\pi$  channel corresponding to m = 1 is populated in first approximation. This gives an asymmetry parameter of -1 (Greene 1980). The hyperspherical adiabatic value is found to be 0.5 and experiment obtains 0.0 at the threshold for exciting the n = 2 levels. Again, allowing for the known 1.7% admixture of the  $\{1,0\}^-$  brings the adiabatic value down to 0.0 in agreement with experiment (Starace and Macek 1987).

The crossing at R = 7 between the  $\{0,1\}^+$  and the  $\{1,0\}^-$  curves is critical for the anisotropy parameters. This crossing between '+' and '-' curves also occurs for the higher *n* levels as seen in Fig. 4. The simple theory using only the dominant  $\{0,1\}^+$  channel has been used to compute the asymmetry parameter for states up to n = 10 by Greene (1980) and the results are shown in Fig. 5 together with the measurements of Heimann *et al.* (1986). Agreement for the higher levels with the hyperspherical adiabatic predictions is good, but there is a hint of disagreement at n = 6. The hyperspherical result slowly approaches the DESB and MO prediction of  $\beta = -1$  as *n* increases, reflecting the increasing importance of the electric field term in equation (2) relative to the angular momentum term for high Rydberg states. The anisotropy of the excited states has been further probed experimentally for the n = 2 levels by Jimenez-Meir *et al.* (1986). The measured anisotropy is also in moderate agreement with the simple adiabatic theory (Greene 1988).

## 3. Concluding Remarks

The adiabatic picture, while quite good at low *n*, is expected to fail for high *n*, since the Rydberg levels crowd together and adiabatic evolution is unlikely. For sufficiently high *n* the double ionisation threshold is approached where two electrons emerge in the Wannier configuration (Fano 1983). Here the electrons always remain on opposite sides of the nucleus so that  $\mathbf{r}_1 = -\mathbf{r}_2$ . We expect that the channels at intermediate distances look something like this configuration. Such states can only be formed by dynamical linear combinations of a large number of adiabatic states. In this case the simple adiabatic evolution that we have described is inappropriate and an entirely new representation is needed.

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## References

Burgdörfer, J. (1983). Z. Phys. A 309, 285.

Fano, U. (1983). Rep. Prog. Phys. 46, 97-165.

Fano, U. (1987). Comments At. Mol. Phy. 19, 253-60.

Feagin, J. M., and Briggs, J. S. (1986). Phys. Rev. Lett. 57, 984-7.

Greene, C. H. (1980). Phys. Rev. Lett. 44, 869-71.

Greene, C. H. (1988). In 'Fundamental Processes of Atomic Dynamics' (Eds J. S. Briggs, H. Kleinpoppen, and H. O. Lutz), pp. 177-96 (Plenum: New York).

Heimann, P. A., Becker, U., Kerkhoff, H. G., Langer, B., Szostak, D., Wehlitz, R., Lindle, D. W., Ferrett, T. A., and Shirley, D. A. (1986). *Phys. Rev.* A **34**, 3782-91.

Herrick, D. R. (1975). Phys. Rev. A 12, 413-24.

Herrick, D. R. (1978). Phys. Rev. A 17, 1-10.

Jimenez-Meir, J., Caldwell, C. D., and Ederer, D. L. (1986). Phys. Rev. Lett. 57, 2260-3.

Lin, C. D. (1984). Phys. Rev. A 29, 1019-33.

Macek, J. H. (1968). J. Phys. B 1, 83-43.

Starace, A. F., and Macek, J. H. (1987). Phys. Rev. Lett. 22, 2385.

Woodruff, P. R., and Samson, J. A. R. (1982). Phys. Rev. A 25, 848-56.

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