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INVESTIGATION OF GENERALIZED OVERLAP AMPLITUDES VIA  $(e,2e)$  SPECTROSCOPY

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INVESTIGATION OF GENERALIZED OVERLAP AMPLITUDES VIA (e,2e) SPECTROSCOPY

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ABSTRACT

The (e,2e) reaction has previously been shown to be an extremely direct and accurate measure of the overlap of the wave function of a target molecule with that of different resolved electronic states of the positive ion resulting from electron knockout. The present paper discusses the reaction in relation to the direct computation of the structure overlaps for different ion states as the generalized overlap amplitudes appearing in the spectral resolution of the one-particle Green's function. The case of water is used to illustrate the effectiveness of the Green's function technique for calculating (e,2e) cross sections for the principal ion states and the use of the reaction as a very sensitive measure of the long-range charge density.

## INTRODUCTION

(e,2e) spectroscopy measures the momentum space overlap amplitude of target and ion wave functions for resolved electronic energy levels of molecular ions [1]. It does this by a kinematically-complete measurement in an ionizing collision initiated by an electron. Not only is the spectrum of the one-electron separation energy  $\epsilon$  measured, but for each ion energy level the profile of recoil momentum  $q$  is obtained for values of  $q$  ranging from zero upwards.

With a suitable choice of collision geometry and a large enough incident electron energy the reaction mechanism is well described by an impulse approximation. The recoil momentum profile may be interpreted directly as the spherically-averaged profile of the squared overlap amplitude in momentum space.

As a first approximation one may interpret the momentum profile for each ion state in terms of the independent-particle model as the spherically-averaged momentum density for the Hartree-Fock orbital of the target system that is associated with the ion state. However, more exactly, if relaxation and correlation effects are allowed for, the overlap amplitudes for different ion states are the generalized overlap amplitudes which appear in the spectral resolution of the one-particle Green's function.

In this paper we express the (e,2e) cross section in terms of a many-body calculation using the Green's function formalism. We investigate the relative importance of (i) relaxation and correlation effects and (ii) the quality of the atomic basis employed when computing the Hartree-Fock wave functions for the water molecule. In doing so we also examine the nature

of the generalized overlap amplitudes and the validity of using the simple molecular orbital interpretation of the (e,2e) cross section.

In a previous paper [2] the (e,2e) experiment on water was described and discussed in relation to molecular orbitals. The present paper is the first to apply in detail the Green's function formalism to (e,2e) spectroscopy.

## 2. THEORETICAL BACKGROUND

Much of the background theory of the (e,2e) reaction on molecules has been discussed elsewhere [1,3]. It will be summarized here.

The basic reaction formalism is the distorted-wave off-shell impulse approximation [1]. However for molecules there is great difficulty in applying an optical model to the calculation of appropriate distorted waves. Furthermore there is little point in such a calculation. Investigation of many cases of small molecules has shown that at high enough incident energy it is sufficient to use an eikonal approximation which represents the distorted waves by attenuated plane waves or, equivalently, by plane waves and an overall attenuation factor  $R$  which is independent of the ion state under investigation, for valence states.

For molecules the Born-Oppenheimer approximation is made and the vibrational average is represented by calculating the electronic wave functions  $|G\rangle$  and  $|F\rangle$  of the target ground state and final ion state respectively using the equilibrium molecular geometry. These approximations have been tested in detail in the case where they would be most expected to break down, that of  $H_2$  and  $D_2$  [4]. They proved valid.

The (e,2e) cross section is given by

$$d^3\sigma/dEd\Omega_A d\Omega_B \propto R|T|^2 \sum_{\mu_r} \int d\Omega \left| \int d^3r \exp(i\mathbf{q}\cdot\mathbf{r}) (F|G\rangle \right|^2. \quad (1)$$

The subscripts A and B label the electron detectors, T is the appropriate half-off-shell element of the Mott scattering t-matrix for the two electrons, which is essentially independent of the variable azimuthal angle  $\phi$  in the noncoplanar symmetric geometry used for this article. The quantum number  $\mu_r$  labels different degenerate states belonging to the same irreducible representation r of the molecular point group.

With the assumption that the (unknown) electron attenuation factor R is independent of the separation energy  $\epsilon_F$  for the final state |F), the (e,2e) cross section is directly proportional to the spherically-averaged absolute square of the Fourier transform of the one-electron overlap amplitude (F|G) with respect to the measured recoil momentum q.

In the extreme independent-particle approximation for target and ion structure, the one electron overlap amplitude is the molecular orbital of the ejected electron. If we allow for correlation and relaxation effects (F|G) is the generalized overlap amplitude of quantum chemistry [5]. The generalized overlap amplitudes, usually denoted for ion states s by  $g_s$ , appear (together with the corresponding functions  $f_t$  for electron attachment) in the spectral resolution of the single particle propagator or Green's function. The (e,2e) formalism of equation (1) directly associates them with the elementary process of ionization.

3. CALCULATION OF THE GENERALIZED ELECTRON OVERLAP AMPLITUDE VIA MANY-BODY TECHNIQUES.

The Fourier transform of the one-particle propagator obeys the equation of motion [6]

$$G_{pq}(E) = \langle\langle a_p^\dagger; aq \rangle\rangle_E$$

$$= E^{-1} \{ \langle [a_p^\dagger, a_q]_+ \rangle + \langle\langle a_p^\dagger; [a_q, H]_- \rangle\rangle_E \}, \quad (2)$$

where the annihilation and creation operators ( $a_q$  and  $a_p^\dagger$ ) obey the anticommutation relations:

$$[a_p^\dagger, a_q]_+ = a_p^\dagger a_q + a_q a_p^\dagger = \delta_{pq} \quad (3)$$

and H is the hamiltonian written in second quantized form:

$$H = \sum_{pq} \langle p|h_1|q \rangle a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} \langle pq|h_{12}|sr \rangle a_p^\dagger a_q^\dagger a_r a_s. \quad (4)$$

The spin orbitals p, q etc. form an orthonormal set. We consider the coordinate space representation of these orbitals.

It is convenient to introduce the field operator

$$\phi(1) = \sum_p a_p p(1) \quad (5)$$

associated with the complete set of spin-orbitals  $\{p(1)\}$ . It is thus possible to define a Green's function:

$$G(1,1';E) \equiv \langle\langle \phi^\dagger(1); \phi(1') \rangle\rangle_E$$

$$= \sum_{pq} p(1)^* q(1') \langle\langle a_p^\dagger; a_q \rangle\rangle_E \quad (6)$$

which has the spectral resolution:

$$G(1,1';E) = \sum_s \frac{g_s(1)g_s^*(1')}{E+E_s^{(N-1)}-E_0^{(N)}} + \frac{f_s(1)f_s^*(1')}{E+E_0^{(N)}-E_s^{(N+1)}}. \quad (7)$$

It is evident that this expression has poles at  $E = E_0^{(N)} - E_s^{(N-1)}$  associated with ionization potentials, and at  $E = E_s^{(N+1)} - E_s^{(N-1)}$  associated with electron affinities.

The generalized overlap amplitudes for the target ground state 0 and the final ion state s

$$g_s(1) = \langle \psi_s^{(N-1)} | \phi(1) | \psi_0^{(N)} \rangle \equiv (F|G),$$

$$f_s(1) = \langle \psi_0^{(N)} | \phi(1) | \psi_s^{(N+1)} \rangle \quad (8)$$

do not form an orthonormal set, but have physical significance as they are directly associated with the elementary process of ionization or electron attachment. They are also related to the natural orbitals of the N-electron system via a canonical transformation [7].

Following Pickup and Goscinski [6], by considering the set of spin-orbital electron field operators  $\underline{a} = \{a_s\}$ , we can write

$$\underline{G}(E) = (\underline{a} | (\hat{E}\hat{1} - \hat{H})^{-1} | \underline{a}). \quad (9)$$

Approximating the superoperator resolvent  $(\hat{E}\hat{1} - \hat{H})^{-1}$  via inner projection techniques [6] yields:

$$\underline{G}(E) = (\underline{a} | \underline{h}) (\underline{h} | \hat{E}\hat{1} - \hat{H} | \underline{h})^{-1} (\underline{h} | \underline{a}), \quad (10)$$

where  $\underline{h}$  is a projection manifold from our operator space of Fermion-like

operators. A particular choice of  $\underline{h}$  consists of the union of the two subspaces [6]

$$\begin{aligned} \underline{h}_1 &= \{a_i\}, \{a_a\} \text{ for } i \leq N \leq a, \\ \underline{h}_3 &= \{a_a^\dagger a_i a_j\}, \{a_i^\dagger a_a a_b\} \text{ for } i < j \leq N < a < b, \end{aligned} \quad (11)$$

where the spin-orbital field operators are associated with a Hartree-Fock (HF) basis and the following conventions have been adopted:  $i, j$  denote hole states,  $c$  denotes the characteristic orbital, i.e. the one from which an electron is ejected,  $a, b$  denote particle states and  $p, q$  denote unspecified spin-orbitals. These specifications of the subscripts guarantee that the basis will be linearly independent. When the  $N$ -electron ground state average is restricted to the HF ground state, we obtain:

$$\begin{aligned} (\underline{h}_1 | \underline{h}_3) &= (\underline{h}_3 | \underline{h}_1) = 0, \\ (\underline{h}_1 | \underline{h}_1) &= 1 \text{ and } (\underline{h}_3 | \underline{h}_3) = 1, \end{aligned} \quad (12)$$

and the following expression is readily derived from partitioning of matrices:

$$\underline{G}^{-1}(E) = (\underline{h}_1 | E\hat{1} - \hat{H} | \underline{h}_1) - (\underline{h}_1 | \hat{H} | \underline{h}_3) (\underline{h}_3 | E\hat{1} - \hat{H} | \underline{h}_3)^{-1} (\underline{h}_3 | \hat{H} | \underline{h}_1). \quad (13)$$

In the HF basis

$$(\underline{h}_1 | E\hat{1} - \hat{H} | \underline{h}_1)^{-1} = \frac{\sum_{pq} \epsilon_{pq}}{E - \epsilon_p}.$$

The simplest non-trivial approximation to equation (13) is obtained by replacing  $\hat{H}$  in the inverse matrix  $(\underline{h}_3 | E\hat{1} - \hat{H} | \underline{h}_3)^{-1}$  by the Fock superoperator  $\hat{F}$ , which is defined by the equation



$$\hat{F} X = [X, F],$$

$$F = \sum_p \epsilon_p a_p^\dagger a_p, \quad (14)$$

where the  $\epsilon_p$  are HF eigenvalues.

For the general spin-orbitals  $p$  and  $q$  we then obtain

$$\begin{aligned} [G^{-1}(E)]_{pq} &= (E - \epsilon_p) \delta_{pq} - \frac{1}{2} \sum_{iab} \frac{\langle ab || pi \rangle \langle qi || ab \rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b} \\ &\quad - \frac{1}{2} \sum_{ija} \frac{\langle ij || pa \rangle \langle qa || ij \rangle}{E + \epsilon_a - \epsilon_i - \epsilon_j} \end{aligned} \quad (15)$$

where the two-electron molecular integrals are defined as

$$\langle pq || rs \rangle = \iiint p^*(1) q^*(2) h_{12} (1-p_{12}) r(1) s(2) d^3 r_1 d^3 r_2, \quad (16)$$

and  $p_{12}$  permutes the coordinates of electrons 1 and 2.

At this stage we make the approximation of associating a generalized overlap amplitude with a particular characteristic orbital  $c$ . The overlap amplitude  $g_{cs}$  associated with the ionization of orbital  $c$  to the ion state  $s$  may be expanded in terms of the complete set of spin orbitals

$$\begin{aligned} g_{cs}(1) &= \langle \psi_{cs}^{(N-1)} | \phi(1) | \psi_0^{(N)} \rangle \\ &= \sum_p C_{cp}^s p(1). \end{aligned} \quad (17)$$

The coefficients appearing in the expression above may be obtained perturbationally since:

$$\begin{aligned} g_{cs}^*(1) g_{cs}(1') &= \frac{1}{2\pi i} \int_{\rho_s} G(1, 1', \omega) d\omega \\ &= \frac{1}{2\pi i} \int \sum_{pq} p^*(1) q(1') G_{pq}(\omega) d\omega, \end{aligned} \quad (18)$$

where  $\rho_s$  is a contour enclosing only the pole  $\epsilon_s$ .

In the case where the many correlated states  $\psi_{cs}$  with the same symmetry as the orbital  $c$  are dominated in a localised energy region by one state whose coefficient  $C_{cc}^s$  is large, we perform the contour integration round the nearby Koopmans pole  $\epsilon_c$ . If we expand the expression for the Green's function (equation 9) about the Koopmans poles we obtain the expression:

$$G_{pq}(\omega) = \frac{\delta_{pq}}{\omega - \epsilon_p} + \frac{1}{\omega - \epsilon_p} \left\{ \frac{1}{2} \sum_{ija} \frac{\langle ij || pa \rangle \langle aq || ij \rangle}{\omega - \epsilon_i - \epsilon_j + \epsilon_a} + \frac{1}{2} \sum_{abi} \frac{\langle ab || pi \rangle \langle qi || ab \rangle}{\omega - \epsilon_a - \epsilon_b + \epsilon_i} \right\} \frac{1}{\omega - \epsilon_q} + \text{higher order terms,} \quad (19)$$

which may be integrated term by term along  $\rho$ . The residues occurring at the poles  $\omega = \epsilon_p, \epsilon_q$  are

$$\begin{aligned} \text{Res}(\epsilon_p) &= 1 - \frac{1}{2} \sum_{ija} \frac{|\langle ij || pa \rangle|^2}{(\epsilon_p + \epsilon_a - \epsilon_i - \epsilon_j)^2} \\ &\quad - \frac{1}{2} \sum_{abi} \frac{|\langle ab || pi \rangle|^2}{(\epsilon_p + \epsilon_i - \epsilon_a - \epsilon_b)^2} \quad \text{for } p = q, \\ &= \frac{1}{2} \sum_{ija} \frac{\langle ij || pa \rangle \langle qa || ij \rangle}{(\epsilon_p + \epsilon_a - \epsilon_i - \epsilon_j)(\epsilon_p - \epsilon_q)} \\ &\quad + \frac{1}{2} \sum_{abi} \frac{\langle ab || pi \rangle \langle qi || ab \rangle}{(\epsilon_p + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_p - \epsilon_q)} \quad \text{for } p \neq q. \end{aligned} \quad (20)$$

Using the expansion for  $G_{pq}(\omega)$  and these residues we obtain the following expressions for the coefficients  $C_{cp}^s$ :

$$C_{cc}^s = 1 - \frac{1}{4} \sum_{ija} \frac{|\langle ij || ca \rangle|^2}{(\epsilon_c + \epsilon_a - \epsilon_i - \epsilon_j)^2} - \frac{1}{4} \sum_{abi} \frac{|\langle ab || ci \rangle|^2}{(\epsilon_c + \epsilon_i - \epsilon_a - \epsilon_b)^2}$$

$$C_{cp}^s = \frac{1}{2} \sum_{ija} \frac{\langle ij || ca \rangle \langle pa || ij \rangle}{(\epsilon_c + \epsilon_a - \epsilon_i - \epsilon_j)(\epsilon_i - \epsilon_p)} + \frac{1}{2} \sum_{iab} \frac{\langle ab || ci \rangle \langle pi || ab \rangle}{(\epsilon_c + \epsilon_i - \epsilon_a - \epsilon_b)(\epsilon_c - \epsilon_p)},$$

(p ≠ c). (21)

If we remove the approximation of associating a generalized overlap amplitude with a particular characteristic orbital c, equation (21) includes a sum over c.

These expressions may also be derived by writing the ground state and ionised state wave functions as configuration-interaction wave functions including all double and single excitations. Hence the expression

$$\langle F | G \rangle = \sum_p C_{cp}^s p(1) \tag{22}$$

is employed in the many-body computation of the generalized overlap amplitude. This expression takes into account correlation and relaxation effects via the terms appearing in the expressions for the coefficients  $C_{cp}^s$  (equation 21).

The equations developed in this section indicate that the generalized overlap amplitudes obtained by contour integration contain rather detailed information, even though the approximations are developed from the Hartree-Fock N-particle ground state. This phenomenon of 'correlation feedback' is an essential feature of the propagator formalism.

#### 4. THE SPECTROSCOPIC SUM RULE.

In previous (e,2e) analysis [1] the use of the sum rule

$$\sum_s S_{cs} = 1 \tag{23}$$

for spectroscopic factors (defined in reference [1]) has proved vital as a confirmation of the general validity of the spectroscopic interpretation of the data. This rule has been derived with the approximation that the target ground state is uncorrelated (i.e. represented by the Hartree-Fock determinant).

In terms of the Green's function formalism the exact sum rule is obtained from the one-particle density matrix [7],

$$\gamma(1|1') = \sum_s g_s(1) g_s^*(1'). \quad (24)$$

The trace of  $\gamma(1|1')$  must be the total number of electrons in the target system.

Since, in the Born-Oppenheimer approximation, wave functions belonging to different irreducible representations of the molecule point group are independent, we find a sum rule of the form

$$\sum_{sc} \int d^3r_1 |g_{cs}(1)|^2 = \sum_c N_c, \quad (25)$$

where the  $c$  label the different characteristic orbitals belonging to the same representation, and  $N_c$  is the occupation number of the orbital  $c$ .

The  $(e,2e)$  momentum profile for an ion state  $s$  usually distinguishes the corresponding characteristic orbital  $c$ . In this work we assume that there is a characteristic orbital associated with an ion state. (The situation where an ion state is characterized by more than one Hartree-Fock orbital belonging to the same representation is discussed in the configuration interaction picture for the case of CO by Dey et al. [3]).

With the characteristic orbital  $c$  distinguished experimentally, the sum rule becomes

$$\sum_s \int d^3r_1 |g_{cs}(1)|^2 = N_c. \quad (26)$$

In terms of spin orbitals  $p, q$  the sum rule becomes

$$\sum_s \sum_{pq} \int d^3r_1 C_{cp}^S * p^*(1) C_{cq}^S q(1) = N_c. \quad (27)$$

Using the orthonormality of the spin orbitals, this becomes

$$\sum_s \sum_p |C_{cp}^S|^2 = N_c. \quad (28)$$

In cases, such as the water molecule, where the off-diagonal  $C_{cp}^S$  are small (usually less than 1% of  $C_{cc}^S$ ), the (e,2e) cross section is essentially proportional to  $[C_{cc}^S]^2$ . We call this the spectroscopic factor  $S_{cs}$ .

The spectroscopic sum rule (28), neglecting off-diagonal  $C_{cp}^S$ , becomes

$$\sum_s S_{cs} = N_c. \quad (29)$$

## 5. BASIS SETS

Two basis sets were employed in these calculations. The first is the Snyder and Basch [9] (4s, 2p/2s) basis, and the second is the Dunning [10] (5s, 3p/3s) basis. The generalized overlap amplitudes were computed only using the larger (5s, 3p/3s) basis.

## 6. RESULTS AND DISCUSSION

### a) The effect of different basis sets

In figure 1 we have shown the experimental values obtained at 400eV

and 1200eV for the angular correlations of the four valence orbitals for water together with the theoretical profiles computed from:

- (i) The Fourier transforms of the Snyder-Basch molecular orbitals obtained from a (4s, 2p/2s) basis (profile A),
- (ii) The Fourier transforms of the Dunning molecular orbitals obtained from the (5s, 3p/3s) basis (profile B), and
- (iii) The Fourier transform of the generalized overlap amplitudes obtained from the (5s, 3p/3s) basis (profile C).

Comparison of profiles A and B shows the effect of increasing the size of the atomic basis set, in particular of adding longer-range orbitals. Much better agreement for the  $1b_1$ ,  $3a_1$  and  $1b_2$  orbitals is obtained for low recoil momenta  $q$  using the longer-range basis. This means that there is a higher electron density at large distances from the nuclei than allowed by the smaller basis set. For the  $1b_1$  orbital, agreement is still not satisfactory at low  $q$ . This is a strong indication that still longer-range terms need to be included in the basis set. This is one of the first indications of the value of the (e,2e) reaction in determining details of charge density.

Comparison of profiles B and C gives an indication of the importance of correlation and relaxation effects.

b) Correlation and relaxation effects

The one-electron generalized overlap amplitude is given by the expression

$$\mathcal{G}_{CS}(1) = \sum_p C_{cp}^S p(1) , \quad (30)$$

where  $\{p(1)\}$  is the set of molecular spin orbitals used as a basis.

In the case of water, this is the complete set of molecular spin-orbitals obtained from the atomic (5s, 3p/3s) basis.

If no relaxation or correlation effects are included, i.e. we employ the target Hartree-Fock approximation and neglect all configuration interaction, then  $C_{cc}^s = 1$  and  $C_{cp}^s = 0$  (all p) so that

$$g_{cs}(1) \equiv c(1). \quad (31)$$

Hence, in this case, the generalized overlap amplitude is just the spin-orbital  $c(1)$  from which the electron was ejected.

In the general case however,  $C_{cc}^s \neq 1$  and  $C_{cp}^s \neq 0$ . In table 1 we have summarized the values obtained for  $[C_{cc}^s]^2 = S_{cs}$  for the principal states  $s$  of water, that is the ones with the largest coefficient  $C_{cc}^s$  in the neighbourhood of the Koopmans pole  $\epsilon_c$ .

It is evident from the table that for the "outer" valence orbitals for water ( $1b_1$ ,  $3a_1$  and  $1b_2$ ) ranging in energy from 14-20eV, the generalized overlap amplitude consists mainly of the original spin-orbital from which the electron was removed together with a small contribution from other spin-orbitals. However for the deeper (37eV)  $2a_1$  level, the spectroscopic factor is approximately 20% smaller than for the outer levels, indicating an increase in importance of relaxation and correlation effects for this level. This result is consistent with what one might expect for more tightly bound levels, since pair correlation energy increases for more tightly bound electrons and the creation of a hole in a deeper level would be expected to result in greater "shake up" and relaxation processes, than would the removal of an outer electron.

For the inner shell principal  $1a_1$  level, relaxation and correlation effects become very much more important, as is indicated by the small value obtained for the spectroscopic factor in table 1.

In the experiment the relative intensities at  $q \geq 0.8$  a.u. of the  $1b_1$ ,  $3a_1$  and  $1b_2$  principal levels are consistent with the assumption that they correspond to nearly equal spectroscopic factors, which we call 0.9 in view of table 2. The intensity of the principal  $2a_1$  level corresponds to a spectroscopic factor of  $0.67 \pm 0.07$ , which agrees with the factor 0.714 of table 1.

In determining the spectroscopic strength of the principal  $2a_1$  level, all the spectroscopic strength in the region of separation energies between 28 and 39eV was included. The separation energy spectrum for this level peaks at approximately 32.5eV and is quite broad, having a high energy tail [2]. Structure is observed up to separation energies exceeding 70eV, and as discussed by Dixon et al. [2], most of this structure can be assigned to the  $2a_1$  orbital on the basis of its dependence on the momentum  $q$ . At  $q = 0.4$  a.u. and 0.7 a.u. the high energy strength amounts to respectively to  $(25 \pm 5)\%$  and  $(31 \pm 6)\%$  of the main  $2a_1$  peak.

It is possible that some of the spectroscopic strength not included in the principal levels for the  $1b_1$ ,  $3a_1$  and  $1b_2$  orbitals has been included in the experimental data for these levels shown in figure 1, since the experimental energy resolution [2] is insufficient to discriminate against small contributions from neighbouring ionic levels other than the principal levels. This would have the effect of raising the curves obtained from the generalized overlap amplitude (by a maximum of 10%), or alternatively of decreasing the relative magnitude of the calculated principal  $2a_1$  cross section.



7. CONCLUSIONS

The (e,2e) reaction is extremely sensitive to details of the shapes of molecular orbitals. It is particularly sensitive to low momentum components and thus provides a sensitive measurement of electron charge density far from the nuclei. This is illustrated particularly for the  $1b_1$  orbital of water.

It is a direct measurement of the generalized overlap amplitude in momentum space. This provides much detail about relaxation and correlation effects, particularly for deeper energy levels where these effects can be large. This is illustrated in the present case by the  $2a_1$  orbital.

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DIFFERENTIAL CROSS SECTION (ARBITRARY UNITS)

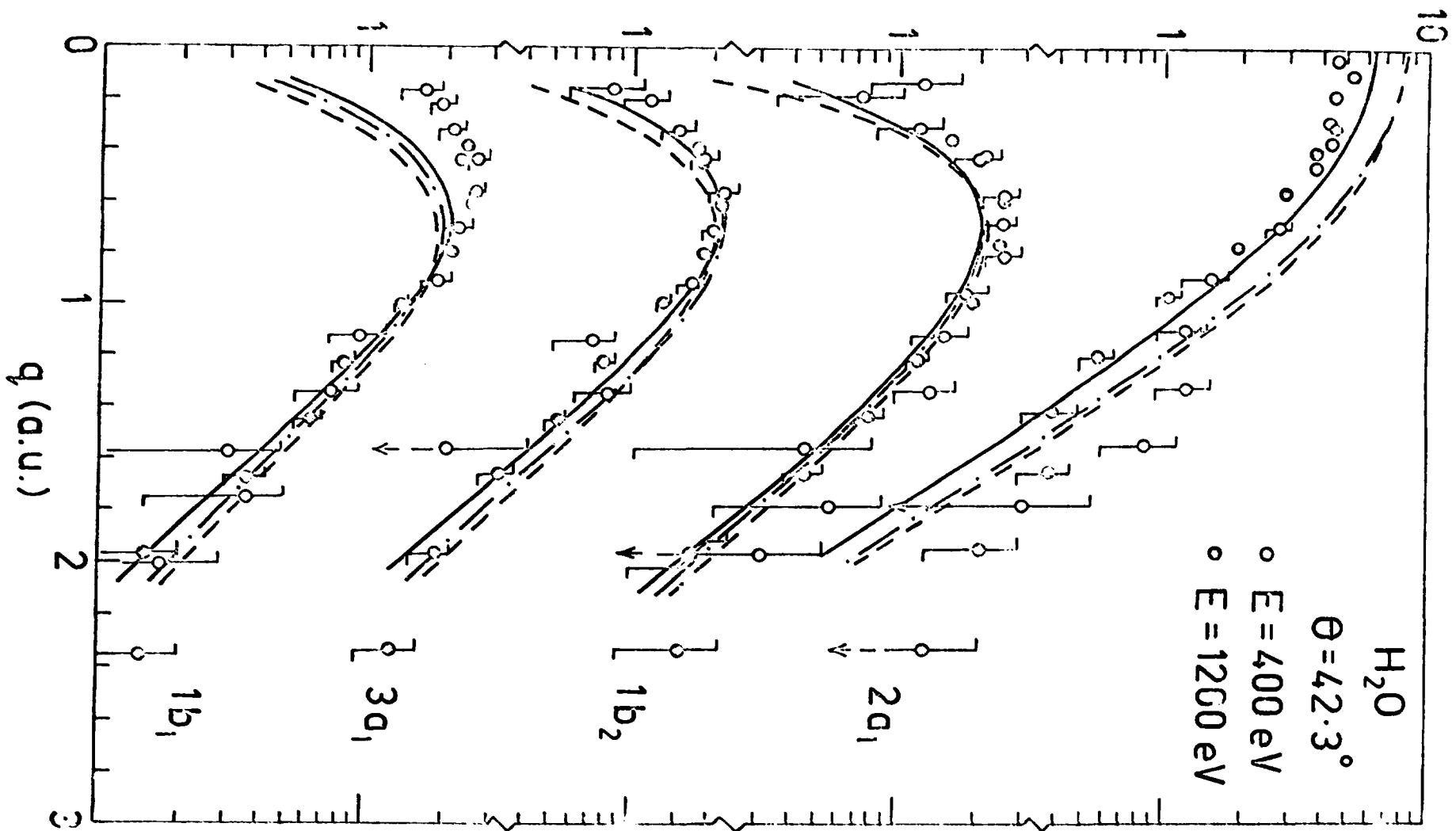


TABLE 1.

Theoretical orbital energies and Spectroscopic factors for the principal ion states of the water molecule.

<u>Orbital</u>	<u>Orbital energy (<math>\epsilon_c</math>)</u>	<u><math>S_{cs}</math></u>
1b <sub>1</sub>	13.90eV	0.868
3a <sub>1</sub>	15.55eV	0.877
1b <sub>2</sub>	19.60eV	0.907
2a <sub>1</sub>	37.20eV	0.714
1a <sub>1</sub>	559.67eV	0.383

Figure 1.

The noncoplanar symmetric ( $e, 2e$ ) differential cross sections at 400eV ( $\circ$ ) and 1200eV ( $\circ$ ) for the principal valence orbital transitions in  $H_2O$  plotted as a function of the recoil momentum  $q$ . The curves show the plane wave calculations using: (A) the molecular orbital wave functions of Snyder and Basch [9] (- - - -); (B) Dunning molecular orbitals [10] obtained from the (5s, 3p/3s) basis (—.—.) and (C) the generalized overlap amplitudes obtained from the (5s, 3p/3s) basis (——). The cross sections for the different transitions are determined relative to each other, the absolute magnitude is not measured. The calculated cross sections have the experimental angular ( $\alpha$ ) resolution folded in. For low  $q$  the curves B and C are indistinguishable for the  $3a_1$  and  $1b_2$  transitions.

