Investigations of Molecular Orbitals with Accel-Decel Beams

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BNL--35312

DE85 005128

Invited Talk, Presented at
Eighth Conference on the
Application of Accelerators in Research and Industry
Denton, Texas
November 12-14, 1984

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ABSTRACT

Quasimolecular transition energies can be found directly from the impact-parameter dependence of interference structure observed in measured K x-ray spectra. As these experiments require a K-vacancy bearing projectile at collision velocities small compared to the equivalent K-shell electron velocity, the accel decel technique has to be used. Such an experiment was performed at the BNL Tandem Accel-Decel Facility for collisions of Cl^{16+} with Ar at energies ranging from 2.5 to 20 MeV. A new method of analysis using the uniform asymptotic approximation is described here. Quasimolecular transition energies derived using this method are compared to results of a previous analysis based on the determination of the relative positions of maxima and minima in the interference patterns.

*Work supported by Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy under Contract No. DE-AC02-76CH00016.

1. INTRODUCTION

Spectroscopy of continuum x rays emitted during slow ion-atom collisions can provide valuable information about the formation of transient quasimolecular orbitals (MO). In particular, if a K x-ray measurement is performed under single collision conditions, and if the projectile brings a K-shell vacancy into the collision, then the $1s\sigma-2p\pi$ MO transition energies can be determined from an analysis of the x-ray spectra [1,2].

The analysis relies on the fact that for any x-ray energy the observed transition can occur either on the incoming or the outgoing part of the collision trajectory. Therefore, the transition matrix element is a sum of two terms with equal amplitude and with a well-defined phase difference, and the interference between these two terms creates an interference pattern of maxima and minima in the measured x-ray spectra (For example see fig. 1 and [1,2]).

This interference pattern depends both on the MO transition energy as a function of the internuclear separation, R , and on the actual time dependence of R , which can be accurately determined under single-collision conditions. Therefore, in principle, a correlation between specific values of R and of the MO transition energy can be established through an appropriate study of interference patterns. The Stationary Phase Approximation (SPA) provides a convenient approach for such an undertaking.

In a previous paper [2], an analysis using SPA was based on extracting the relative positions of maxima and minima from measured

K x-ray spectra for $\text{Cl}^{16+} + \text{Ar}$ collisions at energies of 2.5, 5, 10, and 20 MeV. Accel-decel beams from the Brookhaven National Laboratory Tandem Van de Graaff Heavy Ion Source [3] were used to obtain the almost fully-stripped projectiles at velocities which were low enough to allow the formation and study of quasimolecular orbitals.

In the earlier effort [2], the $1s\sigma-2p\pi$ transition energies were obtained for R from 2500 to 7000 fermi. Energy values for smaller R could not be obtained as this scheme of analysis provides MO energies only for R much greater than the distance of closest approach.

An alternative approach developed here is to use Airy analysis, derived from the Uniform Asymptotic Approximation (UAA), which is an extension of SPA [4]. Instead of estimating the relative positions of maxima and minima, the Airy analysis provides a method of extracting information from the behavior of the measured spectra near the high energy "tail". Therefore, it can provide MO energies near the distance of closest approach. For the $\text{Cl}^{16+} + \text{Ar}$ spectra $1s\sigma-2p\pi$ transition energies were obtained for values of R from 500 to 3000 fermi, thus extending significantly the results of the previous analysis.

This paper is devoted to the description of the Airy analysis and its results. The underlying mathematics is described in Sec. 2 and 3, and the analysis scheme is discussed in Sec. 4.

2. Stationary Phase Approximation (SPA)

The dipole transition matrix element for a transition between two time dependent states has been calculated by Weiskopf [5] using the WKB approximation. He finds

$$D(\omega) = \frac{1}{2\sqrt{2\pi}} \int_{-\infty}^{\infty} D(R(t)) \exp(i \int_0^t (\omega - \bar{\omega}(s)) ds) dt \quad (1)$$

where $D(R(t))$ is the time dependent dipole matrix element and $\bar{\omega}(t)$ is the time dependent energy difference between the two states.

$D(\omega)$ can be evaluated [2] using the stationary-phase approximation (SPA). However, this approximation breaks down for $\omega \approx \bar{\omega}(0)$, i.e., near the classical cutoff frequency. A modification of the SPA can be applied in this region, but it will be valid only for a narrow range of ω . Fortunately another approximation scheme exists [4], which combines the merits of both the regular and the modified SPA and allows us to evaluate $D(\omega)$ both close to and far from $\omega \approx \bar{\omega}(0)$. This scheme will be discussed in the next section.

For the regular SPA consider the integral

$$J(\omega) = \int_{-\infty}^{\infty} g(t) \exp(i f(\omega, t)) dt \quad (2)$$

where $f(\omega, t)$ is a linear function of the parameter ω and the following conditions are satisfied:

(a) $g(t)$ is an even function of t .

(b) $f(\omega, t)$ is an odd function of t (which means that f'' is also odd while f' is even).

(c) $f'' > 0$ for $t > 0$, and $f'' < 0$ for $t < 0$, i.e., f' has a single minimum at $t = 0$.

It is also assumed that for some range of the parameter ω , the SPA equation

$$f'(\omega, t) = 0 \quad (3)$$

has real roots. Using the substitution

$$f(\omega, t) \leftrightarrow \int_0^t (\omega - \bar{w}(s)) ds \quad (4)$$

$$g(t) \leftrightarrow \frac{1}{2\sqrt{2\pi}} D(R(t))$$

it is easy to check that conditions (a)-(c) are satisfied by the functions in (1). The range of ω for which (3) has real roots is $\omega_\infty < \omega < \bar{w}(0)$ when ω_∞ is the asymptotic value of $\bar{w}(t)$ for $t \rightarrow \pm \infty$.

Using standard SPA [4], $J_k(\omega)$, the contribution from the surroundings of any root t_k of eq. (3) to $J(\omega)$ is given by

$$J_k(\omega) = \left(\frac{2\pi}{|f''(t_k)|} \right)^{1/2} g(t_k) \exp \left[i(f(\omega, t_k) + \frac{\pi}{4} \operatorname{sgn} f''(t_k)) \right] \quad (5)$$

Assuming that ω is in the proper range, eq. (3) has exactly two real roots (a result of conditions (b), (c) above), t_1 and t_2 , where

$t_1 > 0$ and $t_2 = -t_1 < 0$. Also, it follows from the symmetry properties of f and g that the contributions from t_1 and t_2 are complex-conjugates. Summing both contributions we find

$$J(\omega) \approx 2 \left(\frac{2\pi}{f_1'''} \right)^{1/2} g_1 \cos \left(f_1 + \frac{\pi}{4} \right) \quad (6)$$

It should be noted that the result blows up when $f_1''' \rightarrow 0$. This problem can be traced to the fact that in this case the expansion $f(\omega, t) \approx f(\omega, t_1) + f''(t_1)(t-t_1)^2/2$ which is used in the framework of SPA, is not justified. Assuming that $f'''(t_1) \neq 0$, $J(\omega)$ can still be evaluated using the next cubic term in the Taylor expansion of f . The solution contains Airy functions [4], but the applicability of the approach is limited to a narrow range of ω values.

$D(\omega)$ is obtained from eq. (6) using eq. (4). It results in

$$D(\omega) = \frac{D_1}{(-\ddot{\omega}_1')^{1/2}} \cos \left[\int_0^{t_1} (\omega - \ddot{\omega}(s)) ds + \frac{\pi}{4} \right] \quad (7)$$

The use of SPA in the evaluation of (2) is justified when t_1, t_2 are far enough apart, so that their contributions to the integral can be evaluated independently and when $g(t)$ is slowly changing around t_1, t_2 . Those statements can be formulated quantitatively as

$$\frac{f_1'''}{t_1^2} \ll 1 \quad (8a)$$

$$\left| \frac{f_1'''}{(f_1'')^2} \frac{g'}{g} \right| \ll 1 \quad (8b)$$

The derivation of these results, which is straightforward but tedious, will not be given here.

When ω is such that $f'(\omega, 0) \rightarrow 0$, both t_1 and t_2 tend to zero. It can be shown that in this case conditions (8a), (8b) usually break down. Keeping in mind that $f''(0) = 0$ identically (see condition (b) above), this breakdown is just another illustration of the fact that SPA cannot be used when the roots of eq. (3) are too close to zeroes of f'' . Inspection of eq. (7) immediately reveals that in our case this forbidden ω region is that of $\omega \sim \bar{\omega}(0)$, i.e., near the classical cutoff frequency.

3. Uniform Asymptotic Approximation (UAA)

Following Connor [4] a new variable z is introduced.

$$f(\omega, t) = \frac{1}{3} z^3 - \xi(\omega)z + A(\omega) \quad (9)$$

where A and ξ are constants which are chosen so as to make

$$\begin{aligned} t = t_1 &\leftrightarrow z = \xi^{1/2} \\ t = t_2 &\leftrightarrow z = -\xi^{1/2} \end{aligned} \quad (10)$$

and where t_1, t_2 are the roots of eq. (3), as before. It can be shown that A and ξ can be chosen to be positive for real roots and negative for complex t_1, t_2 .

By now we assume that the roots t_1, t_2 are real (and therefore $t_2 = -t_1$). Substituting (10) into (9) and solving for ξ and A we find:

$$A = 0$$

$$\xi = \left(-\frac{3}{2} f_1\right)^{2/3} \quad (11)$$

when the fact that f is odd and $f_1 < 0$ was used.

Now substitution of eq. (9) into (2), and using the results of (11), yields

$$J_1(\omega) = \int_{-\infty}^{\infty} g(t(z)) \cdot \frac{dt}{dz} \exp\left[i\left(\frac{1}{3} z^3 - \xi z\right)\right] dz \quad (12)$$

$g \cdot \frac{dt}{dz}$ can be expanded in powers of z . As any term starting from second order up can be transformed into a combination of zero and first order terms using integration by parts in (12) the expansion can be written as

$$g \cdot \frac{dt}{dz} = p + qz \quad (13)$$

Substituting (10) into (13) and solving for p,q, yields

$$p = \frac{1}{2} g_1 \left(\frac{dt}{dz} \Big|_1 + \frac{dt}{dz} \Big|_2 \right) \quad (14)$$

$$q = \frac{g_1}{2\xi^{1/2}} \left(\frac{dt}{dz} \Big|_1 - \frac{dt}{dz} \Big|_2 \right)$$

Finally, differentiating (9) twice, substituting (10), and using the fact that $f_1' = f_2' = 0$, we get

$$\frac{dt}{dz} \Big|_1 = \frac{dt}{dz} \Big|_2 = \left(\frac{2\xi^{1/2}}{f_1''} \right)^{1/2} \quad (15)$$

and therefore:

$$p = g_1 \left(\frac{2\xi^{1/2}}{f_1''} \right)^{1/2} \quad (16)$$

$$q = 0$$

Substituting into (12) we finally obtain:

$$J(\omega) = g_1 \left(\frac{2\xi^{1/2}}{f_1''} \right)^{1/2} \int_{-\infty}^{\infty} \exp \left[i \left(\frac{1}{3} z^3 - \xi z \right) \right] dz = 2\pi g_1 \left(\frac{2\xi^{1/2}}{f_1''} \right)^{1/2} \text{Ai}(-\xi) \quad (17)$$

It is interesting to check the behavior of (17) for the limiting cases $\xi \gg 0$ and $\xi \ll 0$. Using (11) and the asymptotic form of $A_1(-\xi)$ [4] we get

$$\xi \gg 0 \Rightarrow J(\omega) \approx 2 \left(\frac{2\pi}{f_1'''} \right)^{1/2} g_1 \cos \left(f_1 + \frac{\pi}{4} \right) \quad (18)$$

which is identical with (6). The case of $\xi \ll 0$ which corresponds to complex roots of (3), cannot be derived directly from (17), as (17) itself was derived assuming that the roots are real. However, Connor's procedure can be repeated for this case and the result, up to constant phase, is

$$\xi \ll 0 \Rightarrow J(\omega) \approx \left(\frac{2\pi}{|f_1''|} \right)^{1/2} g_1 \exp[-| \text{Im} f_1 |] \quad (19)$$

Another interesting case is that of $\xi \rightarrow 0$, which corresponds to $f_1'' \rightarrow 0$. Unlike the result of SPA the expression for $J(\omega)$ in (17) converges in this case to a finite limit:

$$\xi \rightarrow 0 \Rightarrow J(\omega) \approx 2\pi g(0) \left(\frac{2}{f_1'''(0)} \right)^{1/3} A_1(0) \quad (20)$$

which is identical to the result of the modified (cubic) SPA.

Now, $D(\omega)$ is obtained from $I(\omega)$ in (17) using the substitution (4), and we get

$$D(\omega) = \left[\frac{\pi \left(-\frac{3}{2} \int_0^{t_1} (\omega - \tilde{\omega}(s)) ds \right)^{1/3}}{-\tilde{\omega}_1} \right]^{1/2} D_1 \text{Ai} \left[-\left(-\frac{3}{2} \int_0^{t_1} (\omega - \tilde{\omega}(s)) ds \right)^{2/3} \right] \quad (21)$$

where the special cases discussed above, i.e., $\xi \gg 0$, $\xi \ll 0$, and $\xi \rightarrow 0$, correspond to $\omega \ll \tilde{\omega}(0)$, $\omega \gg \tilde{\omega}(0)$, and $\omega \rightarrow \tilde{\omega}(0)$, respectively.

4. Discussion

The results of the previous section can be used in analysis of MO x-ray spectra, in two opposite ways. First, theoretical spectra can be calculated using model-derived functions for $D(t)$ and $\tilde{\omega}(t)$ and compared with the experimental data. The second approach is to try to obtain information about $D(t)$ and $\tilde{\omega}(t)$ (especially the last one), using the functional form of $D(\omega)$ from eq. (21) without any a priori assumptions about $\tilde{\omega}(t)$. This second approach has been used in the past [2] and will also be used here.

It has to be remembered that the experimentally measurable quantity is not $D(\omega)$, but the number of photons emitted per unit frequency range, $I(\omega)$ which is given by [6]:

$$I(\omega) d\omega \propto \omega |D(\omega)|^2 d\omega \quad (22)$$

Using $D(\omega)$ from eq. (21) we see that regardless of the specific form of $\tilde{\omega}(t)$, $I(\omega)$ should be an oscillatory function of ω , for $\omega < \tilde{\omega}(0)$. This phenomenon has been indeed experimentally observed [1]. For $\omega > \tilde{\omega}(0)$ eq. (10) predicts an "exponentially"

decreasing behavior. The actual spectrum shape will depend on the function $\bar{\omega}$, and it is not obvious that $I(\omega)$ will actually be an exponential of ω in this region.

It should be obvious that $I(\omega)$ has no end point and extends to infinity. Still, we can regard the point $\omega = \bar{\omega}(0)$ as a "pseudo end point", as it marks the border between the oscillatory behavior for low ω and the monotonically decreasing one for high ω .

Our main interest here is the determination of $\bar{\omega}(0)$, i.e., the energy difference between the two states, from experimental data. In order to achieve this, we compare $I(\omega)$ from eq. (22) with the experimental $I(\omega)$ for ω above the first maximum of the spectrum. As we are dealing with a rather narrow range we will ignore the dependence on ω of all the factors in (21), except for the Airy function which is fast changing. Therefore we get

$$I(\omega) \propto \omega \text{Ai}^2 \left[- \left(- \frac{3}{2} \int_0^{\omega - \bar{\omega}(0)} \text{Ai}^2(s) ds \right)^{2/3} \right] \quad (23)$$

The value ω_1 for which $I(\omega)$ gets its first maximum is to a good approximation also the maximum of the Airy function, and therefore

$$\frac{I(\bar{\omega}(0))}{I(\omega_1)} \cdot \frac{\omega_1}{\bar{\omega}(0)} \approx \left[\frac{\text{Ai}(0)}{\text{Ai}(-x_1)} \right]^2 = 0.44 \quad (24)$$

where x_1 is the first maximum of $\text{Ai}(-x)$. Using (24) it is possible to determine $\bar{\omega}(0)$ simply by inspecting a plot of $I(\omega)/\omega$ in the region above ω_1 , and finding the location at which $I(\omega)/\omega$ drops to 0.44 of its value at the first maximum, as is shown in fig. 2.

Fig. 3 shows the results from this and the previous procedures for the $\text{Cl}^{16+} + \text{Ar}$ data [1,2] at 2.5, 5, and 10 MeV. Note first that as indicated above, the present analysis yields results for smaller values of R than the earlier work [2]. Fortunately, R values between 2500 and 3000 fermi are covered by both approaches. Note the good agreement between the extracted values of quasimolecular transition energies in the region of overlapping R values. This agreement between results obtained using different approximations and derived from different portions of the spectra indicates the reliability of both schemes, each in its own useful range. It also shows that both methods should be used in combination, so as to extract maximal amount of information from the experimental data.

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FIGURE CAPTIONS

Figure 1. Typical MO x ray spectrum [1,2].

Figure 2. Expanded portion of the spectrum from fig. 1 divided by the MO X-ray energy E_x . Application of the Airy analysis method is indicated (see text). The upper horizontal line represents the peak height. The lower horizontal line is located at 0.44 peak height and its intercept with the measured spectrum yields $\tilde{\omega}(0)$, the MO transition energy at closest approach distance. The shaded areas represent experimental uncertainties.

Figure 3. MO transition energies ΔE versus internuclear separation R , obtained using recent (full symbols) and previous (open symbols) analysis. Note the good agreement in the region of overlapping R values.

Figure 1

Figure 2