Space and Time Correlation in High Velocity Multiple Electron Transitions.*

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Abstract

In collisions of high velocity projectiles of charge Z and velocity v, perturbations expansions in Z/v usually converge when $Z/v<1$. Under these conditions Z^3 contributions to cross sections for two electron transitions (e.g. double excitation) may arise if there is interference between first order and second order contributions to the probability amplitude. Non-zero Z^3 terms in two electron excitation or ionization cross sections occur if spatial electron correlation is present. For double excitation non-zero Z^3 contributions require a correlation in time as well. This time correlation corresponds to quantum time ordering arising from virtual off-energy-shell intermediate states. As with second order amplitudes for Thomas singularities in single electron capture, the energy non-conserving amplitude is connected to the energy-conserving amplitude in second order in Z by a dispersion relation. Generalization to higher order transitions (e.g. triple excitation) is discussed.

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Higher order terms in perturbation expansions contain information absent in simpler first order terms. While first Born contributions are useful in evaluating basic cross sections for excitation of a single atomic electron by a high velocity projectile of charge Z, higher order terms in Z are required for either: i) multiple excitation in the absence of correlation, or ii) understanding the nature of intermediate states of the collision. Leading higher order contributions to observable excitation scattering probabilities and cross sections vary as Z^3. These higher-order Z^3 terms contain information about how a scattering event proceeds, information not included in the simpler first-order Z^2 terms. For example, both time ordering[1] and intermediate energy-non-conserving contributions[2] are present only in higher order amplitudes. This information is needed to characterize few and many-body processes in scattering of atoms by fast charged particles. Specifically, we demonstrate that a non-zero Z^3 contribution in single and double excitation cross sections requires the presence of time ordering effects. For double excitation, electron correlation is also necessary[3] for the Z^3 term to be non-zero.

The probability amplitude for a transition from |i> to |f> in scattering a particle of charge Z from an atom may be expressed[3] in the interaction representation as

$$a = <f| \ T \ \exp(\ i\int V(t)dt) \ |i>. \tag{1}$$

Here T is the time ordering operator[1] and V contains a sum of Coulomb interactions between the projectile and each of the electrons in the atom,

namely $V(t) = \sum_j e^{-iH_0 t} \dfrac{Z}{|\vec{R}(t) - \vec{r}_j|}$. The perturbation (or Born) expansion in Z

is given[3] by

$$a = \langle f|i \rangle - i \int_{-\infty}^{\infty} dt \, \langle f|T \, V(t)|i \rangle$$

$$+ \frac{(-i)^2}{2} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt' \, \langle f|T \, V(t) \, V(t')|i \rangle + \ldots . \tag{2}$$

where V is linearly proportional to Z.

The zeroth order term, i.e. $\langle f|i \rangle$, vanishes since the states are orthonormal. In the first order term the time ordering operator plays no role since only one time is involved and T may be replaced by unity. For single or double excitation all integrals over t are purely real. The first order term is zero for double excitation if there is no correlation. Then V is a sum of

single electron operators and $\quad \langle f|V|i \rangle = \sum_j (\phi_k^f \phi_j^f |V(r_j)| \phi_k^i \phi_j^i) - (\phi_k^f|\phi_k^i) = 0 \quad$ for

orthogonal states.[4] In general we may represent the first order term for double excitation in Eq. (2) by $-ic_1 Z$ where c_1 is a real coefficient which is non-zero only if electron correlation is non-zero.

The second order term in Eq. (2) may be analyzed by setting $T=1+(T-1)$. Here $T=1$ is the limit in which time ordering effects vanish. Hence we define $T-1$ to be the operator which carries the effects of time ordering. Keeping this in mind and using the step function θ, the intermediate state propagator from the $e^{\pm iH_0 t}$ factors between $V(t)$ and $V(t')$ in Eq. (3) is[3]

$$\frac{T}{2} e^{-i\epsilon(t-t')} = \theta(t-t') \, e^{-i\epsilon(t-t')} = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{-i\Omega(t-t')} \, \frac{1}{\Omega - \epsilon + i\eta} \, d\Omega$$

$$= \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{-i\Omega(t-t')} \left\{ -i\pi\delta(\Omega - \epsilon) + P\frac{1}{\Omega - \epsilon} \right\} d\Omega . \tag{3}$$

The principle value term $P\frac{1}{\Omega - \epsilon}$ vanishes in the limit as $T \to 1$. Thus the

$-i\pi\delta(\Omega-\epsilon)$ term in Eq. (5) corresponds to T=1 and the $P\frac{1}{\Omega-\epsilon}$ term corresponds to T-1, which carries the effects of time ordering. We note that in the second order term T-1 may be replaced[1] by $2\theta(t-t') - 1 = 2(\theta-\bar{\theta})$ where $\bar{\theta}=1/2$ so that T-1 corresponds to a time variation of the integrand in Eq.(2) from its average values. In this sense T-1 may be regarded as a time correlation. Using this in Eq. (2) it may be shown that all matrix elements for both single and double excitation are real so that the second order term may be represented by $Z^2(ic_2-\bar{c}_2)$ where $\bar{c}_2$ arises from T=1 in Eq. (3) and c_2 arises from the operator T-1 which gives the effects of time ordering.

Collecting terms, the probability amplitude for double excitation through second order in Z given by Eq. (2) may be expressed as

$$a = -ic_1Z - (\bar{c}_2-ic_2)Z^2 = -i(c_1-c_2Z)Z - \bar{c}_2Z^2 \qquad (4)$$

where all the c's are real. We have seen that a non-zero c_1 carries spatial correlation and a non-zero c_2 carries time ordering. We note that $\bar{c}_2$, which has no time ordering, may carry some electron correlations and does include the lowest order independent electron approximation, where a reduces to a simple product of first order probability amplitudes for double excitation.

Cross sections, σ, and scattering probabilities $|a|^2$, may be expressed by

$$\sigma = \int |a|^2 \, d\vec{B} \simeq \int (c_1^2Z^2 - 2c_1c_2Z^3 + c_2^2Z^4 + \bar{c}_2^2Z^4) \, d\vec{B}$$

$$= C_1^2Z^2 - 2C_{12}Z^3 + C_2^2Z^4 + \bar{C}_2^2Z^4 + O(Z^5) \qquad (5a)$$

where $\vec{B}$ is the impact parameter of the projectile. The difference in double excitation by particles of opposite charge is given by

$$\sigma(-) - \sigma(+) = 4C_{12}|Z|^3. \qquad (6)$$

This is non-zero only if effects due to both spatial correlation (in c_1) and time ordering (in c_2) are present.

The time ordering term c_2 also represents effects of energy non-conservation in intermediate states during the collision. This may be seen in Eq. (3) where T-1 is associated with $P \frac{1}{\Omega-\epsilon}$ which restricts $\epsilon \neq \Omega$ so that intermediate energy is not conserved. The energy non-conserving contributions are purely quantum mechanical and maybe ascribed to virtual intermediate states. Energy-conserving intermediate states, corresponding to the $-i\pi\delta(\Omega-\epsilon)$ terms in Eq. (3), also contribute to the double excitation probabilities and cross sections for the $\bar{c}_2$ terms. The energy conserving terms may be directly related to on-shell physically observable processes, and are also present in classical calculations. It may be shown that c_2 and $\bar{c}_2$ obey a dispersion relation so that in the second order amplitude the energy-non-conserving (time-ordered) contribution may be expresses as a integral over energy-conserving (non-time-ordered) contributions and vice versa, namely,

$$c_2(\epsilon) = -\frac{i}{\pi} P \int \frac{\bar{c}_2(\Omega)\, d\Omega}{\Omega-\epsilon} \qquad (7a)$$

$$\bar{c}_2(\epsilon) = +\frac{i}{\pi} P \int \frac{c_2(\Omega)\, d\Omega}{\Omega-\epsilon} \; . \qquad (7b)$$

Such a dispersion relation has been found to hold in the vicinity of a Thomas singularity in electron capture in a calculation[6] using Schrödinger representation.

Our analysis gives some insight into the nature of Z^3 terms in double excitation. However, this analysis does not explicitly distinguish between various specific physical mechanisms such as shakeoff, TS1, polarization, et al.[7-12] which have been proposed to explain observations. In our opinion this question of the specific nature of the mechanism for double excitation is still both interesting and open.

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We have evaluated (4) using correlated configuration interaction (CI) wave functions for the initial and final states. The effective charge Z_{eff} of the helium atom was varied to minimize the ground-state energy. For $Z_{eff}=1.76$, the initial state wave function, $|i) = 0.9916|1s^2> - 0.1251|1s2s> - 0.0230|2s^2> + 0.0251|2p^2>$, gives an energy within 1.6% of the exact energy. The final states were $(2s2P(^1P)| = 1.<2s2p|$, and $(2P^2(^1D)| = 1.<2P^2|$.

In arriving at the second-order amplitudes in (4), we have inserted a complete set of 2-electron, correlated states in (2), have performed the energy decomposition (3), and then have used an average-energy approximation to perform the sum by closure. We chose the degenerate energy $\bar{E}$ of the intermediate states to be 51.8 eV above the ground state. An argument in support of choosing the intermediate-state energy to be in the range of the singly-ionized states is that these are precisely the states that play the major role of interfering with the bound states (at about 60 eV above the ground state) in the observation process.

Cross sections for projectile-impact excitation into the $(2s)^2(^1S)$ state are shown in Figure 1. The proton/antiproton ratio is a factor about 0.8 in the projectile energy region of 0.1 to 0.3 MeV/amu but increases to almost 1 at 1.5 MeV/amu where Giese, et al.[14] made their observation with protons and electrons. Also shown are the close-coupling calculations of Fritsch and Lin[15] at 1.5 MeV/amu. Observations of Pedersen and Hvelplund[16] are consistent with Giese, et al., but have large error bars. One may see that our result is almost all first-order at 1.5 MeV/amu, so the difference in magnitude from experiment is not due to our use of a closure approximation. Since this result is very sensitive to the 1s2s contribution to the ground-state wave function, inclusion of additional bound and continuum states to the wave function may make a difference.

Our results use configuration-interaction bound state wave functions with real coupling coefficients. It is not clear to us that these terms remain real for continuum states. Hence here we avoid analysis of important data for double ionization. Our analysis may be applied to single excitation with the understanding the c_1 is generally non-zero with or without electron correlation. Hence for a non-zero Z^3 term, time ordering is essential in a single excitation cross section, but electron correlation is not.

For higher order terms in Z it is evident that odd Z contributions to $|a|^2$ disappear when energy-non-conserving virtual intermediate states are eliminated since even and odd terms in Z contributing to the amplitude a then differ by a factor of i from the even terms. Also in higher (n>2) order terms time ordering and intermediate energy non-conservation are not in one-to one correspondence. Energy non-conservation introduces a relative phase factor of i every time it occurs. The nth order term contains n-1 propagators any one of which may, or may not, be off the energy shell. Higher order terms in Z are generally required when the condition that Z/v<1 is not met. However, for a group of independent or uncorrelated electrons with similar principal quantum numbers, if the number of electrons is large then products of first order amplitudes are, nevertheless, sometimes sufficient.[13] However, further understanding of the pattern of time-ordering and energy-non-conservation in higher order terms in Z remains open to further investigation.

In the independent electron approximation the lowest order non-zero term for an N electron transition is a product of N first order transitions. That is, Nth order perturbation theory is approximated by a product of N first order transitions. This is a significant reduction in complexity. This result is changed when the projectile carries electrons since interactions between target and projectile electrons can excite both electrons. If multi-

electron effects are weak then the first N-1 amplitudes for an N electron transition may be small since these terms go to zero as multi-electron effects vanish. In this limit the leading order term in Z_P/v is the nth order independent electron approximation term. As the strength of electron correlation is increased or the collision velocity is increased, the first N-1 terms become relatively more important.

In summary, we have shown that Z^3 contributions to atomic excitation contain time ordering contributions from the Z^2 amplitude. These time ordering contributions may also be regarded as contributions from energy-non-conserving intermediate states of the collision. For double excitation correlation must be present, in addition to time ordering, for a non-zero Z^3 term to occur. Proton vs. antiproton cross sections for double excitation into the $2s^2(^1S)$ state differ by about 20% in the energy region between 0.1 and 0.3 MeV/amu. At higher collision energies, proton-antiproton differences are smaller.
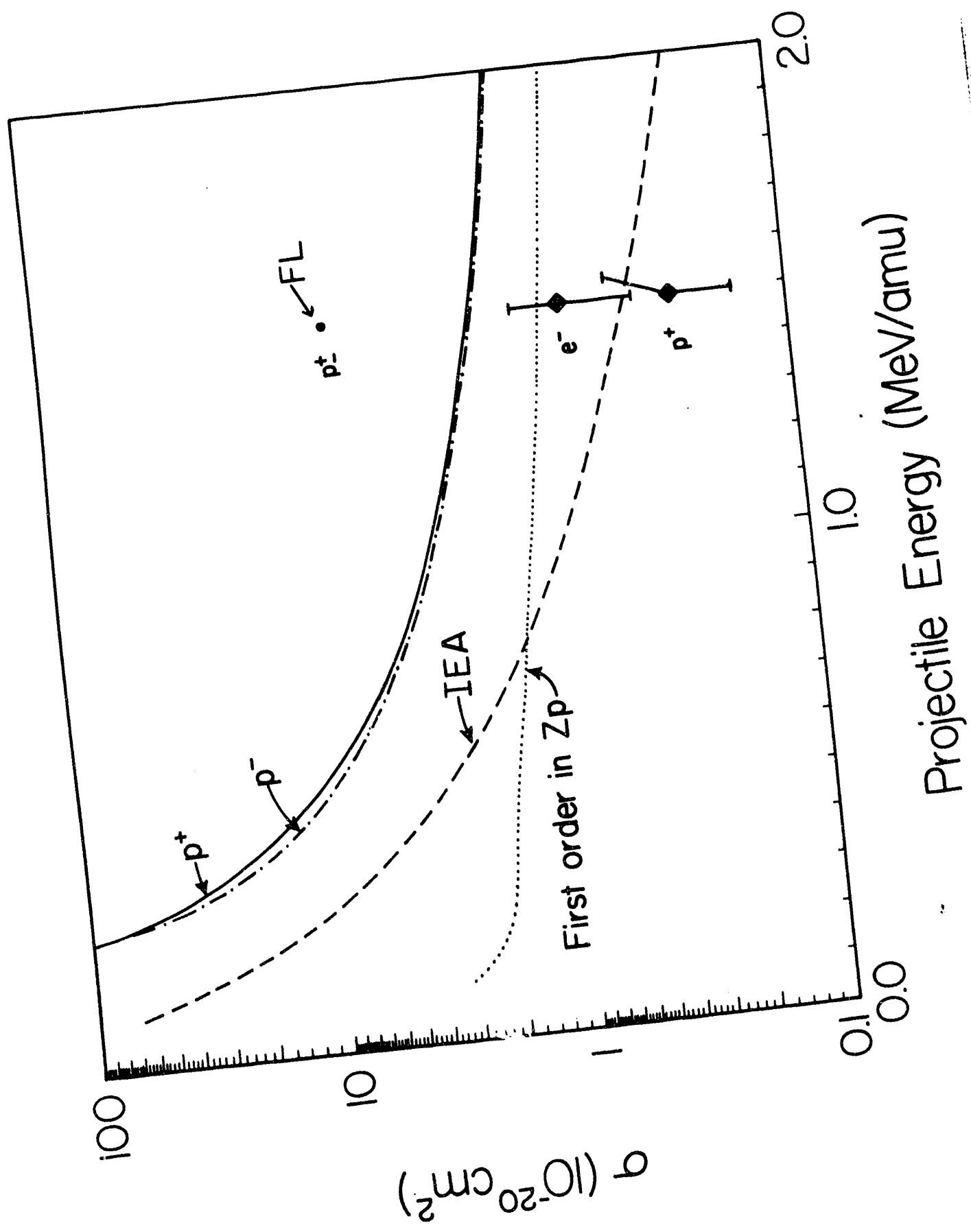
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Figure Caption

Fig. 1. Cross sections for the excitation of helium into the $(2s)^2(^1S)$ state. The solid curve is the second-order result for protons and the dot-dash curve is for antiprotons. The first-order (dotted curve) and (uncorrelated, energy-conserved second order) Independent Electron Approximation (dashed curve) are also shown. FL are the close-coupling result of Fritsch and Lin. The experimental results are from Giese, *et al*.

Projectile Energy (MeV/amu)

σ $(10^{-20} cm^2)$

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