K-SHELL IONIZATION IN COLLISIONS

OF HEAVY ATOMS

by

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SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE JOINT

DEGREE OF BACHELOR OF SCIENCE AND

MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May 12, 1972

Signature redacted

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            Department of Physics, May 12, 1972

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        Chairman, Departmental Committee on Graduate Students

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ABSTRACT

The excitation mechanism is shown in a simple way
to be short range. The standard semi-classical impact
parameter treatment is discussed. The two state approxima-
tion, the Landau Zener theory of level crossing, the per-
turbed stationary state methods, and their relationship to
the adiabatic approximation are discussed in the context of
low energy collision analysis. The Born approximation and
the distortion approximation are discussed as treatments
valid for high energy collisions. (All treatments appear
in their semi-classical form.) A scaling law applicable to
most of these treatments is developed and its relative
merits and shortcomings are discussed. A general discussion
of when the various approximations are valid follows. It is
shown that high (low) energy approximations are valid for
projectile velocities significantly greater (less) than the
orbital velocities of the target electron. The perturbed
stationary state method is shown to be the only applicable
approach ot vacancy production of K-shells in collisions
between heavy ions. Feasibility of computer solutions is
discussed. By considering the assymptotic limits of the
transition probabilities for arbitrary processes in the
limits of very small and very large projectile velocities,
a qualitative sketch of the cross-section for vacancy pro-
duction as a function of collision energy is obtained.

Thesis supervisor: Professor Leo Sartori
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ACKNOWLEDGEMENTS

I.   INTRODUCTION

Throughout most of the literature on atomic collision theory, an atomic collision is generally conceptualized as a point charge projectile scattering off a target atom. In fact, most of the experiments performed in this field up until the last five years used either electrons, protons, or alpha particles as projectiles. In recent years, there have been numerous experiments[1,2,3] in which both the targets and the projectiles were heavy atoms. In dealing with this situation theoretically, one treats the projectile atom as a modification of a point charge. In fact, as we will show later on, when treating K-shell excitation and ionization of a target, a heavy atom projectile can be very well approximated by a point charge.

The projectile can be modeled as a plane wave, or as a classical particle, following a well-defined trajectory, with a definite impact parameter. In the latter case, the treatment is referred to as being semi-classical, as opposed to a strict quantum mechanical treatment. The semi-classical treatment is far more simple from a mathematical point of view. It can be partially justified for all of the cases we deal with, and rigorously justified in the limit of high projectile energies.

In all of our discussion, we will be primarily concerned with inelastic scattering cross-sections. It is useful to know the range of impact parameters which contribute to inelastic processes. While this can be determined by detailed calculations, we present an easy way of showing that it is on the order of the radius of the shell being excited. It is this fact which enables us to approximate a heavy projectile as a point charge in calculating K-shell ionization cross sections.

There are basically two ways of modeling the Hamiltonian felt by the target electron. In the high energy limit, the most viable scheme is to treat the projectile as a small perturbation which vanishes at t=±∞. This can be done as long as the projectile does not significantly distort the wave function of the target atom, and high energies are characterized in this way. Otherwise one must consider a total Hamiltonian containing the potential formed by the Coulomb fields of both the target and the projectile. Clearly this Hamiltonian is time dependent, but the interaction, characterized by an overlap of the two Coulomb fields, is of finite duration. Fortunately, there are approximations which enable one to solve the time dependent Hamiltonian problem in the low energy limit. In this paper, we give a brief survey of both the high energy and low energy approximations, and semi-quantitive discussion of when the various approximations are valid.

The next problem on the agenda is the issue of scaling laws. One might ask, if we know the cross-section for a process in a hydrogen-hydrogen collision as a function of energy of the projectile, can we scale the results to determine the cross-section (as a function of energy) of the same process for say, a uranium-uranium collision? The presence of screening electrons in heavy atoms renders an otherwise elegant scaling law. However, the scaling can be used to approximate results, and in addition, to determine when various approximations should be used. In this paper, we use these scaling laws to show that even for high energy collisions, if the target atom is heavy enough, a particular low energy approximation, (the perturbed stationary state approximation) can be implemented. As this approximation is very difficult mathematically, and not applicable to light targets, there is very little literature on it. The feasibility of solving this problem on a computer is discussed, but inasmuch as no computations were carried out for this research, we can only give a semi-quantitative description of the results. In particular, we discuss the asymptotic behavior of the cross-section in the low and high energy limits.

1. Mathematical Description

In order to write down an atomic collision mathematically, one must decide how to describe the projectile. It must be determined whether the projectile must be treated as a plane wave, or whether semi-classical approximation will suffice. If a classical description of the projectile is to be sufficient, then the minimum uncertainty in its position allowed by a well-specified velocity must be small compared to the characteristic range of the interaction. (The range of the interaction is defined to be the impact parameter of the projectile beyond which the target would not feel its presence appreciably.)

To estimate the range of the interaction, we can specify the perturbation experienced by the target atom for any specified impact parameter of a classical particle. We show that in general, the range of the interaction is on the order of the average radius of the initial atomic state, which for convenience, we will assume to be its ground state.

Of all the multipole components the dipole component can be expected to have the longest range, and we consider this component. The contribution from any given impact parameter can be estimated using the Weizacker-Williams method of virtual quanta.[4] In this method we treat the dipole component of the pulse as being composed of virtual photons, and the transition to a higher state is reduced to the problem of absorption of photons and photo-ionization.

(Since magnetic transitions do not contribute to these processes appreciably, it is sound to treat the pulse in this way.) Here we only need to use the fact that the probability of a certain process taking place is proportional to the number of virtual photons impinging on the aton with energy corresponding to that which is absorbed by the electron in that process.

The center of the atom feels electric pulses, of two polarizations, which, for the dipole approximation, are assumed to be uniform over the range of the atom. For non-relativistic velocities,

$$E_1(t) = \frac{qb}{(b^2+v^2t^2)^{3\,2}} \qquad E_2(t) = \frac{qvt}{(b^2+v^2t^2)^{3\,2}} \qquad (1)$$

$$I_1(\omega,b) = \frac{c}{2\pi} |E_1(\omega)|^2 \qquad (2a)$$

$$\left.\begin{matrix} I_1\,(\omega,b) \\ \\ I_2\,(\omega,b) \end{matrix}\right\} = \frac{1}{\pi^2}\ \frac{q^2}{c}\ \left(\frac{c}{v}\right)^2\ \frac{1}{b^2}\begin{cases} (\frac{\omega,b}{v})^2 K_1^{\ 2}\ (\frac{\omega b}{v}) \\ \\ (\frac{\omega b}{v})^2 K_o^{\ 2}\ (\omega b/v) \end{cases} \qquad (2b)$$

where K_o and K_1 are the standard modified Bessel functions, (I_1+I_2) is roughly constant over all frequencies up to v/b, then drops off sharply.

A trivial calculation shows that for projectile velocity (v) equal to the average orbital velocity (v_o) of an electron in the ground state of an atom with atomic number Z,

$$v/v_o = 2\ I \qquad (3)$$

where I is the ionization potential, and v_o is the Bohr radius of the ground state.

Clearly, this implies that the interaction is short range for that particular velocity.

Due to the fact that $I(w,b) \propto \dfrac{1}{b^2}$, it is easily shown that even for hydrogen, the dipole interaction is of short range for non-relativistic velocities. It can be assumed that the higher order multipole components of the interaction are characterized by an even shorter range. For heavier atoms, the interaction can only become more localized, and in virtually every realistic circumstance, the range of the interaction is on the order of the radius of the atomic shell. This is a very useful result, because in treating collisions between heavy atoms for their resultant K-shell vacancy production cross-section, we can model the projectile as a point charge. This is because the screening of the projectile nucleus by its own electrons is neglegible at internuclear distances equal to or less than the radius of the K-shell of the target.

A necessary condition for treating the projectile classically is that an uncertainty in the position which is small compared to the dimensions of the K-shell does not destroy the information known about the velocity of the projectile.

The radius of the K-shell of a target atom is given by $\tilde{} a_0/Z_{TARGET}$. The corresponding minimum uncertainty in the velocity of the projectile is given by

$$\frac{h}{(\Delta x)(m)} = \frac{(h)(Z_{TARGET})}{(a_0)(m)}$$ where m is the mass of the projectile.

Compatibility occurs for trajectories in which the velocity is much greater than $\Delta v = \dfrac{(h)(Z_{TARGET})}{(a_0)(m)}$.

If we speak of projectiles which have charge comparable to that of the target nucleus, then $\Delta v = \dfrac{(h)(Z_{TARGET})}{(a_0)(2m\ proton)(Z_{proj})}$

$$\approx 10^5 \ cm/sec$$

(4)

and the velocity beyond which the projectile can be treated classically becomes a universal result.

As we will see later, the restriction that the projectile has charge comparable to that of the target nucleus is highly significant, because this is exactly the point at which strict quantum mechanical treatment becomes very difficult.

The matter is not rigorously settled because there is no reason to believe that the position-momentum uncertainty product is always on the order of h at exactly the point where the projectile passes by the target. In fact, the treatment which models the projectile as a plane wave is invariably considered to be more appropriate. One can only make a hand-waving argument that the results are similar providing the velocity is great enough. One can also make the observation that the higher the velocity of the projectile, the greater the position-momentum uncertainty product compatible with a classical description.

It has in fact, been proven by Moisewitch,[5] Crothers and Holt[6] that for high energy approximations, (specifically, the kinetic energy of the projectile must be much greater than the energy of excitation of the atom) quantum mechanical results approach those of the analogous semi-classical treatment.

II. THEORETICAL BACKGROUND

$$h = e = m_e = a_o = 1$$

The structure of the following discussion will be such that we will start with inelastic collisions of the lowest energies, and work up to the high energy collisions. Following this survey of the various treatments, we will discuss in detail when exactly each of these treatments apply. The discussion will be brief, and the reader is encouraged to check the references if he desires more detail.

First we will discuss the concept of adiabaticity. In the semi-classical model that we are using, the electrons feel a time dependent Hamiltonian $H(t)$. The concept of stationary states thus loses its meaning in this context. In order to find a handle on the problem, one can think of "freezing" the Hamiltonian at any given time. He can then have stationary states corresponding to a frozen Hamiltonian, which in turn, corresponds to the physical situation at time t. These stationary states form a complete set of states, $\{\phi_i(t)\}$ and the true wave function $\psi(t)$ can be expressed in an expansion of the stationary solutions of time t; $\psi(t) = \sum_n a_n(t) \phi_n(t)$.

Now consider the stationary states at any given time.
For a small enough time Δt later, there will be a set of
stationary states $\{\phi_n(t+\Delta t)\}$ which bear a one to one corres-
pondence to the set $\{\phi_n(t)\}$. Furthermore, since the
physical potential has changed only a little bit, the state
$\phi_n(t)$ bears a very close resemblance to $\phi_n(t+\Delta t)$ for all n.
and of course, we can consider the complete set of states
$\{\phi_n(t)\}$ all bearing a distinct one to one correspondence
to $\{\phi_n(t+\Delta t)\}$. Thus we see that if we label a particular
state at time t, we can label the state which it resembles
so closely at time $t+\Delta t$ by the same name so to speak. In
the same manner, we can label the states $\phi_n(t)$, $-\infty < t < +\infty$
by the same name. Thus we can use a formalism in which
although an individual state changes with time, it maintains
a particular identity. The energy corresponding to this
state for instance, may be changing with time, but the energy
curves (energy plotted as a function of time, or as a
function of any variable corresponding directly to time) will
be continuous connected graphs. This is the beauty of the
stationary (otherwise known as adiabatic) states. We can
speak of a particular adiabatic state which bears the same
identity at all times, and we can speak of an energy curve
associated with this state.

It is obvious that if the Hamiltonian is not changing appreciably, then $a_n(t)$ are not changing appreciably either. One might correctly expect that if the Hamiltonian is changing very slowly as in the case of slow, "gentle", atomic collisions, then not only is $\frac{da_n(t)}{dt}$ small, but $\int_{-\infty}^{\infty} \frac{d\ a_n(t)}{dt}\ dt$ is also small. This fact will be justified mathematically later on.

Since the adiabatic states are to be calculated only as a function of internuclear distance, $\phi_n(-\infty)$ and $\phi_n(+\infty)$ turn out to be the same combinations of atomic states, as $|R(t)| = \infty$ in both cases. Hence, given the set of quantities $\{a_n(-\infty)\}$, and $\{a_n(+\infty)\}$ one would know the excitation probabilities.

The processes which occur at arbitrarily low energies are resonance phenomena. The purest example of resonance is resonant charge exchange between two identical atoms.[7] In this process, the electron does not actually get excited to a higher energy state, but merely "latches on" to the ionic projectile as it goes past. If the collision is at such a low energy that the probability of exciting the electron to a higher energy state is neglegible, then we can work in a space of two states; the atomic state in which the electron is bound to the target, and the atomic state with the same energy in which it is potentially bound to the projectile. Consider for example, a proton colliding with a hydrogen atom in the 1S state. At all times, the eigenstates of energy

with which we deal are the bonding and anti-bonding states
of the 1S shell of the atoms, ϕ_1 and ϕ_2.

adiabatic
energies
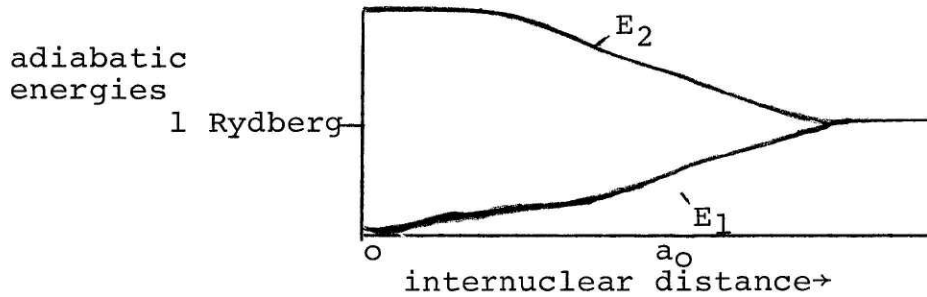
(The 1S state of the projectile at R = ∞
is given by an anti-symmetric combination
of ϕ_1 and ϕ_2.)

The 1S state of the target nucleus at R = ∞ is a symmetric
combination of ϕ_1 and ϕ_2 . At t = +∞, the final state is

$$\psi(+\infty) = \phi_2 + \phi_1 e^{i\int_{-\infty}^{\infty}\varepsilon(t)dt} \quad \text{where } \varepsilon = E_2 - E_1 \quad (4)$$

and the probability for charge exchange is then given by

$$P = \sin^2\left(\frac{1}{v}\int_{-\infty}^{\infty}\varepsilon(R)dR\right) \quad (5)$$

Figure 1 shows the result of this two state approximation
compared to experimental results. Since momentum transfer
has been neglected in this treatment, one would expect it to
over estimate the actual charge exchange cross section when
the projectile velocity becomes significant compared to the

orbital velocity of the electron.

Resonant charge transfer involves resonance between two atomic states. Another form of resonance occurs when a molecular state containing an electron has, for some internuclear separation, the same energy as a vacant molecular state. This internuclear separation at which the energy levels cross is called the "crossing point", and impact parameters less than the crossing point result in what are called "curve-crossing" collisions. This form of resonance is damped by the repulsion of levels due to off-diagonal perturbing matrix elements. A particular theory of level crossing was developed by Landau and Zener[8] in 1932.

First of all, in making a zeroth order adiabatic approximation, one simply assumes that aside from the change in energies associated with them, the stationary states are not changing in time. That is to say, the finite internuclear motion does not significantly couple the adiabatic states. The Landau-Zener model makes this very assumption. Given that $\psi(t) = \sum_n a_n(t)\phi_n(t)$ it also assumes that $a_n \approx 0$ for all but two states, ϕ_a and ϕ_b. The off-diagonal perturbation matrix elements, which cause both the repulsion of levels and the coupling of the states is also assumed to be constant.

These assumptions are justified on the grounds that the transition basically takes place at the crossing point $- R_x$ a very localized region with respect to the spatial dimensions of the system (see Figure 2). The probability of

transition at a crossing point, according to this theory, is $e^{-H^2/\alpha}$ where H is the off diagonal perturbing matrix element, and α is $\left(\dfrac{d\ (E_1-E_2)}{dt}\right)_{R_x}$. The perturbation to which we have been referring is basically everything that was considered in the original calculation of the energy level curves. The problem with the Landau-Zener theory is that it is very hard to determine the matrix elements of this perturbation and in fact the perturbation is sometimes written off as an experimental parameter. Lichten has conjectured that H is of the same order of magnitude as the subshell splitting of the united or separated atomic levels which correspond most closely.

There are many other problems with the Landau-Zener theory, more than time permits to go into, and attempts to improve it continue to this day.

There is a very important approximation which one would describe as a first order treatment above the adiabatic treatment.[9] In this approximation, the perturbation which appeared in the last paragraph is assumed to be neglegible. That is to say, all of the significant coupling between different adiabatic states arise from the finite internuclear motion. This approximation, known as the perturbed stationary state approximation, is in the usual spirit of a first order perturbation treatment, assumes that $a_0(t) \approx 1$ and $a_n(t) \approx 0$ for $n \neq 0$. Again, we expand the true wave functions in terms

of stationary states, and write Schroedinger's equation in this form.

The adiabatic solutions are written as $\psi_s(r,R)e^{i\omega_s(R)t}$ where R denotes the internuclear separation, and r denotes the coordinates of the electron.

$$H\psi_s(r,R) = \varepsilon_s(R)\ \psi_s(r,R) \tag{6}$$

When R is very slowly varying with t, we use solutions of the Schroedinger's equation which are zero-order in the time dependence of the Hamiltonian, namely $\{\psi_s(r,R(t))e^{-i\int_0^t \varepsilon_s(R(t))dt}\}$ as an orthonormal basis. Expanding in terms of these states, we write

$$\psi(t) = \sum_s c_s(t)\ \psi_s(r,R(t))e^{-i\int^t \varepsilon_s(R(t))dt} \tag{7}$$

and substituting into the Schroedinger's equation, we obtain

$$\sum_s (c_s(t)\frac{\partial}{\partial t}\psi_s(r,R(t)) + \frac{dc_s(t)}{dt}\ \psi_s(r,R(t))e^{i\int_0^t \varepsilon_s(R(t))dt} = 0 \tag{8a}$$

Projecting onto the state $\psi_p(r,R(t))e^{i\int_0^t \varepsilon(R(t))\ dt}$

$$\frac{dc_p}{dt} = \sum_s \{c_s(t)\ \int\psi_p^*(r,R(t))\ \frac{\partial}{\partial t}\ \psi_s(r,R(t))\ d^3r\}\ e^{-i\int_0^t \varepsilon_{sp}(R(t)\}dt}$$

where $\varepsilon_{sp}(R(t) = \varepsilon_s(R(t)) - \varepsilon_p(R(t))$

If at $t = -\infty$, the electron is in a particular atomic eigenstate of the target atom A, then to zero-order we assume that $C_n(t) = \delta_{ng}$, and to first order

$$\frac{dc_s}{dt} = <\psi_s^*(r,R(t)) \frac{\partial}{\partial t} \psi_g(r,R(t))> e^{-i\int_o^t \epsilon_{sg}(R(t))dt} \quad dt \quad (9a)$$

or for $s \neq g$,

$$c_s(+\infty) = \int_{-\infty}^{\infty} <\psi_s^*(r,R(t)) \frac{\partial}{\partial t} \psi g(r,R(t))> e^{-i\int_o^t \omega(R(t)dt} \quad dt \quad (9b)$$

In the case where the projectile follows a straight-line trajectory with impact parameter b,

$$c_s(+\infty) = \int_{-\infty}^{\infty} <\psi_s^*(r,b,z) \frac{\partial}{\partial z} \psi_g(r,b,z)> e^{-i/v \int_o^z \omega(b,z)dz} \quad dz \quad (9c)$$

In this form the velocity appears only as a factor in the experiment. It is clear that as $v \to 0$, $C_s(+\infty) \to 0$ due to rapid oscillations in the integral.

It should be pointed out that for simplicity, recoil

of the target nucleus has been ignored, as Schroedinger's equation is presumably valid only in an inertial frame of reference. To take recoil into account, a m dification of the perturbed stationary state method is required, but for the purposes of this paper is unnecessary.

It should also be pointed out that if ψ_g is a target eigenstate at $t=\pm\infty$, then

$$\langle \psi_s^*(r,b,z) \frac{\partial}{\partial z} \psi_g(r,b,z) \rangle = 0$$

at $t = \pm\infty$. This fact will enable us to integrate by parts later on.

Both the Landau-Zener theory and the perturbed stationary state method are suitable for both charge exchange and excitation because in the midst of the collision, the molecular stationary states bear no particular loyalty to either atom. This of course, is because we have ignored momentum transfer during the process of charge exchange. We discuss the issue of momentum transfer briefly later on; but since in this paper we are primarily interested in excitation and ionization, and are only valid when the projectile velocity is much less than the orbital velocity of the electron, we will not discuss the modifications of these approximations which take charge exchange into account.

It should also be noted that when off-diagonal perturbation matrix elements and the finite motion of the nucleus produce the same order of magnitude of coupling, the

analysis becomes extremely difficult. Lichten[10] has discussed the cases of bands of states with very narrow energy separation, but his discussions have been basically qualitative in nature.

The treatment of non-resonant charge exchange involves a much more sophisticated formulation than that of resonant charge exchange. In this case, charge exchange involves an energy change, and cannot take place at arbitrarily slow collision energies. However, if the energy difference between a filled state of one atom ϕ_a, and some vacant state of another atom ϕ_b is small compared to the energy differences between the initial target state and all other possible final states, then there is an energy range in which the projectile velocity is large enough to cause charge exchange, but small enough such that no other states besides ϕ_a and ϕ_b come into play; and once again, we can make a two state approximation.

The true-wave function $\psi(t)$ can be written as the linear combination $a(t)\phi_a(\vec{s}) + b(t)\phi_b(\vec{x})$. Using a variational technique, one can obtain a pair of coupled differential equations in $a(t)$ and $b(t)$
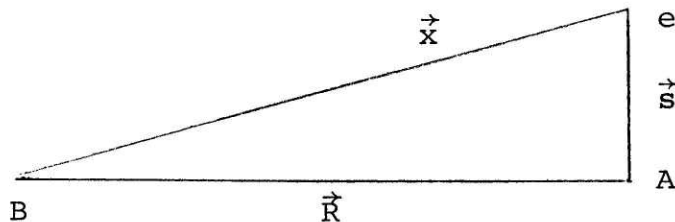
$$V_A = \frac{-1}{s} + \frac{1}{R} \qquad\qquad V_B = \frac{-1}{x} + \frac{1}{R}$$

The derivation of the equations is long and un-interesting.[11] The key concept involved is that the coupling between a and b arises due to the finite overlap of ϕ_A and ϕ_B, $(S_{ab} \equiv <\phi_A / \phi_B> \neq 0)$ finite coupling due to the perturbation V.

$(V_{ab}^{\overset{B}{\underset{A}{}}} = <\phi_a | V_{\overset{B}{\underset{A}{}}} | \phi_b>$

The result is

$$i \begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} + S \begin{pmatrix} ab \\ ba \end{pmatrix} \begin{pmatrix} b \\ a \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} V_{\begin{pmatrix} aa \\ bb \end{pmatrix}}^{\begin{pmatrix} B \\ A \end{pmatrix}} + \begin{pmatrix} b \\ a \end{pmatrix} V_{\begin{pmatrix} ab \\ ba \end{pmatrix}}^{\begin{pmatrix} A \\ B \end{pmatrix}} \tag{10}$$

It is clear that as the energy of the projectile is increased, the two-state approximation becomes poorer and poorer. N-state approximations can be done which are conceptually the same as two state approximations, but which of course are much more difficult. Calculations involving as many as 8 states have been performed.[12]

It should be noted that electron translation factors have not been taken into account in the preceding treatment. Bates and McCarrol[13] have shown that $\psi(r,t) = \phi(v,t) e^{i\nu z - \frac{i\nu^2 t}{2}}$ obeys the equation $(H_{el} - i\frac{\partial}{\partial t})\psi(r,t) = V_T(r,t)\psi(r,t)$ where $V_T(r,t)$ describes the presence of the target nucleus, and H_e is the unperturbed Hamiltonian of the projectile. Bates has also shown that ψ correctly describes the eigen-state associated with the moving projectile at $t = -\infty$.

The formalism of the two state approximation in this case
is exactly the same, but here,

$$S_{ab} = \int d^3r \quad \phi_a \vec{r} \phi_b(\vec{r}+\vec{R}) \ e^{\ i\nu z}$$

$$V_{ab} = \int \phi_a(\mathbf{r}) \ \frac{Z}{|\vec{r}-\vec{R}|} \ \phi_b(\vec{r}+\vec{R}) \ e^{\ i\nu z} \ d^3r$$

When S_{ab} and V_{ab} are small due to rapid oscillations in the
integrands of the integrals that express them. Thus, for
high v, charge exchange starts becoming neglegible. Physically,
the meaning of this is that charge exchange is neglegible
when the translational velocity of the projectile is sub-
stantially greater than the orbital velocity of the electron.

On the other hand, for high velocities, the collision
is capable of exciting the electron to different energy levels
of the target atom. Roughly speaking, one can say that the
energy uncertainty associated with the time duration of the
collision is the same order (or greater) than the energy
difference between the various levels of the target atom,
under the condition that the velocity of the projectile is on
the same order (or greater) than the orbital velocities of
the electron.

$$\Delta\omega = \frac{1}{\Delta t} = Z\nu \gtrsim (Ryd.)Z^2 \ ; \quad \nu > Z = \text{velocity of orbital}$$
$$\text{electron}$$

In this energy range therefore, it is convenient to expand
the true state in terms of unperturbed eigenstates of the
target atom.

The most basic treatment in this realm is the Born approximation. This approximation has been solved thoroughly treating the projectile quantum mechanically.[14] For the sake of continuity however, we briefly summarized the semi-classical equivalent of the Born approximation[15], otherwise known as the impact parameter Born approximation. As mentioned before, it has been proven equivalent to the quantum mechanical treatment at high energies.

$$V_{no}(R) \equiv \int d^3r \, \phi_n(r) \, \frac{1}{|r-R|} \, \phi_o(r) \tag{11}$$

$$a_n(t) = a_n(-\infty) + \int_{-\infty}^{t} V_{no}(R(t)) e^{i\omega t} dt. \tag{12a}$$

Assuming a straight projectile trajectory with impact parameter b,

$$a_n(+\infty) \underset{n \neq o}{=} \int_{-\infty}^{\infty} V_{no}(b,z) e^{\frac{i\omega z}{v}} \frac{dz}{v} \tag{12b}$$

The transition probability $P_n(+\infty)$ is given by

$$P_n(+\infty) = |a_n(+\infty)|^2 \tag{12c}$$

and the cross-section for the transition, σ, is given by

$$\sigma = \int_{o}^{\infty} bdb \, |a_n(+\infty)|^2 \tag{12d}$$

By inspection, one can guess the form of the
results of the Born approximation. When the velocity is
large enough such that $\frac{\omega a}{v} << |$, the term $e^{\frac{i\omega z}{v}}$ is effect-
ively unity, and the cross section goes as v^{-2}. For velo-
cities low enough such that $\frac{\omega a}{v} >> |$, the term $e^{\frac{i\omega z}{v}}$
produces many oscillations in the integrand of the term

$$\int_{-\infty}^{\infty} V(b,z) \, e^{i\omega z/v} \, dz$$

This causes the value of the integral to vanish faster than
any power of v, hence the cross section increases with v at
low velocities. This sort of argument will be presented
in more detail later on. The maximum can be expected to be
roughly at $\frac{\omega}{v} \approx \frac{1}{a}$ or $v \approx \omega a$

i.e. just before rapid oscillations in the integrand begin
to dominate (see Figure 3).

The most elementary modification of the impact
parameter Born approximation is called the distortion
approximation. It merely uses first order energies in the
exponent instead of the zero order energies, i.e.

$$a_n(t) = \int_{-\infty}^{\infty} V_{no}(R(t)) \, e^{i\int_{o}^{t} \omega'(R(t) \, dt} \, dt \tag{13a}$$

where

$$\omega'(R(t)) = \omega + V_{nn}(R(t)) - V_{oo}(R(t))$$

The result is somewhat improved at the expense of a terrific increase in the labor of calculation (see Figure 3). This approximation was actually carried out by Bates[16] for proton on hydrogen collisions.

III. SCALING LAWS

Having described the main methods of solving atomic
collision problems in different energy ranges, we now discuss
scaling laws with which one can scale the velocity of the
projectile, and the charges of both the target and the
projectile concurrently. These laws give us a way to a)
scale results to some degree of accuracy and b) to know how
to model any given situation once the analysis has been done
for, say, hydrogen.

The Born approximation has been scaled in the past,
and we present the analogous semi-classical derivation of
the scaling law.

For the cross section of excitation from state a
to state b, of the target atom, (atom #1).

z_1 = charge of nucleus of atom 1

z_2 = charge of nucleus of atom 2

$$V_{ab}^{1,1}(R) = \int d^3r \quad \phi_a^H(r) \; \phi_b^H(r) \; \frac{1}{|\vec{r} - \vec{R}|} \quad \equiv \quad \text{perturbation}$$

matrix element induced by a proton at distance $\vec{R}$ from a
hydrogen atom. ($\phi_{\substack{a \\ b}}^H$ are ordinary hydrogenic states).

$V_{ab}^{z_1,z_2}(R) \equiv$ perturbation matrix element induced by a point
charge $q = z_2$ near an atom of nuclear charge z_1. Screening
is ignored for now. $a_{ab}^{z_1,z_2}$, the transition amplitude, and

σ^{z_1,z_2} bear the same notational form.

ω_1 is the energy differnece between states a and b of the target atom, and ω_H is ω_1 for the special case of hydrogen. Since screening electrons are ignored for now, $\omega_1 = Z_1^2 \omega_H$.

$$V_{av}^{z_1,z_2}{}'(R) = \int d^3r \phi_a^{(1)}(r)\phi_b^{(1)}(r)\frac{Z_2}{|\vec{r}-\vec{R}|} =$$

$$\int d^3r (Z_1^{3/2}\phi_a^H \phi^H(Z,r))(Z_1^{3/2}\phi_b^H(Z_1,r))\frac{Z_2}{|\vec{r}-\vec{R}|} = \quad (14)$$

$$\int d^3(Z_1 r)\phi_a^H(Z_1 R)\phi_b^H(Z_1 R)\cdot\frac{Z_2 Z_1}{|Z_1\vec{r}-Z\vec{R}|} =$$

$$Z_2 Z_1 \ V_{ab}^{1,1}(Z,\vec{R})$$

$$a_{ab}^{Z_1,Z_2}(b,+\infty,\nu) = \frac{1}{\nu}\int_{-\infty}^{\infty} V_{ab}^{Z_1,Z_2}(x,b)\,e^{i\frac{\omega i}{\nu}x}\,dx$$

$$= \frac{1}{\nu}\int_{-\infty}^{\infty} Z_1 Z_2 V_{ab}^{1}{}^{1}{}'(Z_1 x, Z_1 b)\,e^{i(\frac{\omega_1}{Z_1^2})(\frac{Z_1 x}{\nu/Z_1})}\,dx$$

$$= \frac{Z_2}{(\nu/Z_1)Z_1}\int_{-\infty}^{\infty} V_{ab}^{1\ 1}(Z_1 x, Z_1 b)\,e^{i\omega_H\frac{(Z_1 x)}{(\nu/Z_1)}}\,dZ_1 x$$

$$= \frac{Z_2}{Z_1}a_{ab}^{1,1}(Z_1 b,+\infty,\nu/Z_1)$$

$$(15)$$

$$\sigma^{Z_1, Z_2}_{ab}(\nu) = \int_0^\infty |a^{Z_1 Z_2}_{ab}(b, +\infty, \nu)|^2 (2\pi b)\ db$$

$$= \frac{2\pi}{Z_1^2}\ (\frac{Z_2}{Z_1})^2\ |a^{1,1}_{a,b}(Z_1 b, +\infty, \nu/Z_1)|^2\ (Z_1 b)\ (Z_1 b)$$

$$= \frac{Z_2^2}{Z_1^4}\ \sigma^{1,1}_{ab}(\nu/Z_1) \tag{16}$$

If ϕ_b is a continuum state, say ϕ_K, then to keep proper normalization, we decrease the volume of a hypothetical box enclosing the system by Z_1^3. This preserves the condition $\phi_b(r) = Z_1^{3/2} \phi_b^H(Z, r)$.

When dealing with continuum states, one incorporates a state density term in integrating over the continuum of states. By simple square well analysis, a decrease in the box by a factor of Z_1^3 decreases the number of states with energy between E and E+ΔE by Z_1^3. However, scaling up the energy E to $Z_1^2 E$ for any particular state has the effect of scaling up p(E)dE by a factor of Z_1^3; where p(E) is the number of states per unit energy interval. Hence, the overall scaling operation leaves the density factor untouched.

Thus, the scaling law is the same for ionization, and of course, for total excitation, (excitation plus ionization).

For the distortion approximation, the results scale only if $Z_2 = Z_1$.

Then $\omega'(\vec{R}) = \omega_o' + V_{nn}'(\vec{R}) - V_{oo}'(\vec{R})$

$$= Z_1^2 \, (w_o^H + V_{nn}^H \, (Z\vec{R}) = V_{oo}' \, (Z\vec{R}))$$

and ε' $(bx) \equiv \int_0^x \omega(b,x)dx = Z_1^2 \int_0^{Zx} \omega(Zb,Zx) \, dZx$

$$= Z_1^2 \, \varepsilon^H(Zb,Zx) \tag{17}$$

To scale all of the quasi-molecular models, the same idea is used, but first we must know how to scale the energies of the molecules, as we did with the energies of atoms.

To do this, we note a particular symmetry of the Schroedinger equation, to which one may attribute the nice scaling relationships of atomic wave functions. This symmetry in the Schroedinger equation has nothing to do with the spherical symmetry of the atom per se.

Consider a potential produced by a distribution of Coulomb centers.

$$\frac{1}{2} \frac{\partial^2}{\partial \vec{x}^2} \psi + \sum_i \frac{1}{|\vec{x} - \vec{R}_i|} \psi = E\psi \tag{18}$$

If all the Coulomb centers increase their charge by a factor of Z, and the spatial distribution shrunk by a factor of Z

$$\frac{1}{2} \frac{\partial^2}{\partial \vec{x}^2} \psi' + \sum_i \frac{Z}{|\vec{x}-R_{i/Z}|} = E'\psi' \tag{19}$$

$$= \frac{1}{2} Z^2 \frac{\partial^2 \psi'}{\partial (Z\vec{x})^2} + \sum_i \frac{Z^2}{|Z\vec{x}-\vec{R}_i|} = E'\psi'$$

then $\psi'(x) = \psi(x/Z)$ is a solution with $E' = Z^2 E$.

This nice result is possible because the kinetic energy term is proportional to $(\vec{dx})^{-2}$.

Hence the energy curves of quasi-molecular eigenstates as a function of internuclear distance can be scaled upon multiplying both the target nucleus and projectile charge by Z.

i.e. $E(Z_1\vec{R}) = Z_1^2 E(1, Z_1\vec{R})$

For resonant charge exchange

$$P_{ab}(\nu, Z, b) \quad \sin^2\left(\frac{1}{\nu} \int_{-\infty}^{\infty} \varepsilon(Z,R)\,dr\right)$$

$$= \sin^2\left(\frac{1}{\nu} Z \int_{-\infty}^{\infty} \varepsilon(1,ZR)\,d(ZR)\right)$$

$$= P_{ab}(\nu/Z, 1, b/Z)$$

$$\sigma(z) = \frac{1}{Z^2} \sigma(1) \qquad (20)$$

For the perturbed stationary state method

$$A(\nu, Z, b) = \int_{-\infty}^{\infty} \langle\phi_b| \frac{\partial}{\partial t} |\phi_a\rangle \, e^{i\int\omega(t)dt} \quad dt$$

$$= \int_{-\infty}^{\infty} \langle\phi_b| \frac{\partial}{\partial R} | \phi_a\rangle e^{i\int\frac{\omega(R)}{\nu}\,dR} \quad dr$$

$$(21)$$

$$= \int_{-\infty}^{\infty} \langle\phi_b^H| \frac{\partial}{\partial ZR} | \phi_a\rangle e^{i\int\frac{\omega^H(ZR)dZR}{(\nu/Z)}} \quad dZR$$

$$= A(\nu/Z, 1, Zb)$$

Thus we see that the general scaling law for a particular process is the same regardless of the approximation used. Namely, if the charge, of both the target and projectile nuclei are multiplied by Z, the result for the value of the cross section is Z^{-2} times the cross section in the case of the original charges where the velocity was Z^{-1} times as much.

The neat law is inaccurate for two reasons. In the first place, as Z is increased the target atom gains mote electron which fill up more shells; hecne certain processes possible in light atoms are not possible in heavy atoms. Secondly, screening effects cause the energy between two specified levels to go as less than Z^2. In most cases infact, it is not clear that the scaling argument are valid. (Consider the fact that all atoms are on the order of one angstrom in radius; this clearly shows that scaling outer electronic shells is meaningless.) Nevertheless, K-shells of heavy atoms are not affected severely by outer electrons, and for the most part, they "look like" K-shells of hydrogen; hence in these cases, the scaling law is of some value.

The prime value of the scaling laws at this point is the observation that by the inspection of the Schroedinger equation that we have done, it is not only the mathematics of a particular approximation which follows a scaling law, but rather it is the physics itself which scales. That is

to say, if a person were watching movies of atomic collisions, (say for instance, he was watching hydrogen excitation by protons at various collision velocities), he would have no way of knowing that he was seeing proton-hydrogen collisions as opposed to say He^+ - alpha particle collisions (assuming all trajectories are straight lines) or Ag^{+46} - Ag^{+47} collisions for that matter, without being told the scale of the movie before hand. Thus we can use the scaling relationships to determine which method is appropriate for which situations based only on our knowledge of the relative successes of these approximations in any one given case.

In future notation, a situation having (v, Z_p) as the projectile (velocity, charge), Z_T as the atomic number, and σ as the cross section for a particular process, will be said to have a "universal velocity" of v/Z_T, and a universal cross-section of $Z_T^2 \sigma$.

IV. CHARACTERIZATION OF LOW AND HIGH ENERGIES

Now that a somewhat universal formulation of atomic collision problems has been achieved, we can ask the general question of when to use which approximations.

All of the models we use can be divided into two categories: Those that are a first order calculation of some sort, and those that are exact calculations in an analytic sense, the approximation entered in the modeling per se. In the first category are the Born approximation and all the modifications thereof, and the perturbed stationary state method; in the second category are the Landau-Zener theory of level crossings and the two-state (or n-state) approximation.

It is clear that of any perturbation approach, a necessary condition for the validity is that the probability of excitation is small, and I will not mention this point anymore.

In the Born approximation, the main worry is that the target wavefunctions are distorted by the incoming projectile. This problem can be neglected when a) the velocity of the projectile is large compared to that of the orbital electron, and b) the charge on the projectile is small compared to that of the target nucleus. Henneberg[17] has shown that the joint condition can be expressed mathematically as

$$\frac{Z_{prog}\, e^2}{h\,(\nu)} \ll | \qquad\qquad (22)$$

or in our notation, $\nu \gg Z_{proj}$.

This says in effect, that the universal velocity above which
the Born approximation works is lower for lighter project-
iles.

Figure 4 illustrates the complimentary fact that the
larger the atomic number of the target, the smaller the
universal velocity that can be tolerated in the Born approx-
imation.

For any two state approximation, it is necessary
that no other state play a major role in the process. A
rough characterization of this condition can be given as
follows: There is a characteristic time of the interaction
which is equal to the range of the interaction, (that is,
the diameter Δx of the atomic orbitals) divided by the velocity
of the projectile. This defines a certain characteristic
uncertainty in the energy of the electron $h\nu_{/\Delta x}$. If the
energy separation between atomic levels is large compared to
the uncertainty in the energy of the electron, then roughly
speaking, the two state approximation is valid.

The Landau-Zener theory involves many approximations,
some of which are extremely particular. One of these

approximations however, applies to all methods which expand

in terms of adiabatic molecular solutions. There is however,

an important subtlety which generally receives no attention.

Any approximation which uses an expansion in terms

of adiabatic molecular eigenstates assumes that the true

wave function is composed "mostly" of one or two such

states. This assumption is vulnerable on two distinct

counts. 1) We encounter the same problem as we do for any

first order (or zeroth order) approximation: If the probab-

ility of excitation is too high, then the true wave function

is not represented well by a wave function which represents

the zeroth order wave function in excitation probability.

This is extremely elementary. 2) Regardless of excitation

per se, there is another concept associated with the failure

of the adiabatic approximation. For a quasi-molecule with

finite relative nuclear velocity, one can label the eigen-

states of energy with the usual adiabatic labels, despite the

fact that it is difficult to conceptualize these states.

Simply label state X with the label that one would assign

to the adiabatic state which state X approaches as the relative

nuclear velocity approaches 0. In a near-adiabatic approxi-

mation, in addition to assuming little excitation, one must

necessarily assume that the non-adiabatic state X is roughly

equal to the adiabatic state X. The distinction is usually

vacuous because the presence of appreciable components of

higher energy states in the non-adiabatic state X is synono-

mous with appreciable excitation to these same states. Nevertheless, it is useful to realize the distinction, since in heavy atomic collisions, an electron will find many of the higher states filled, and to first order, could not be excited to these neighboring states. This state under consideration however, would experience the same discrepancy with its adiabatic counterpart regardless of the presence of other electrons. To examine the restriction under which a state is almost equal to its adiabatic counterpart, we consider, for simplicity, an isolated atom moving with velocity v relative to the lab frame. Assume that at a certain time, say t = 0, the atom is centered at the origin. The electronic part of the 1S wave function $\psi(\vec{r},o)$ is then given by $\sum_n c_n \phi_n$ where $\{\phi_n\}$ is the orthonormal basis constituted by the "adiabatic" atomic states - i.e. the states that would be eigenstates if the atom was stationary. The coupling terms

$$<\phi_n | \frac{\partial}{\partial t} \; \psi(r,t)> \text{ getting } \psi(r,t)>_{t=o} \tag{23}$$

where $\frac{\partial}{\partial t}\phi_n = \omega_n \phi_n$ (factor of magnitude unity are ignored).

In the adiabatic approximation we assume that $c_n \approx \delta_{on}$ so that $\psi(r,\Delta t) \approx \phi_o(\vec{r}-\vec{v}\Delta t)$

          so

$$\frac{\partial}{\partial t} \psi(r,t) \approx \vec{v} \cdot \vec{\nabla} \psi(r,t)$$

$$(24)$$

$$\langle \phi \left| \frac{\partial}{\partial t} \psi(r,t) \right\rangle_{t=o} \approx \langle \phi_n \left| \vec{v} \cdot \vec{\nabla} \right. \psi(r,t) \rangle_{t=o}$$

so $\quad c_n \omega_n = \nu \langle \phi_n | \nabla \phi_o \rangle = \frac{\nu}{\Delta z} \langle \phi_n | \cos\theta | \phi_o \rangle \qquad (25)$

where $\theta = (\vec{r} - \vec{v}t) \cdot \hat{z} \qquad \Delta z =$ radius of is wave function

and $\hat{z} = \hat{v}$.

The adiabatic approximation requires that $\sum\limits_{n \neq o} |c_n|^2 \ll |$

If one considers the fact that the magnitude of the electron's orbital z – momentum is $\frac{\sim h}{\Delta z}$ we see that the restriction essentially requires that the translation velocity of the atom be small compared to the magnitude of the z-component of the orbital velocity of the electron, assuming $\sum\limits_{n} \langle \phi_n | \cos\theta | \phi_o \rangle$ is on the order of unity. This then, is equivalent to the Born Oppenheimer approximation. It seems reasonable to generalize this result to $\Delta z = a_o$ and this restriction demands that the velocity of the proton projectile be must less than unity, in atomic units.

A similar way of restricting the velocity is to set the characteristic uncertainty of the energy, (mentioned before), much less than the energy difference of the various levels between which transitions take place. For a proton-hydrogen collision, if the energy difference are one the order of a Rydberg,

$$\nu \ll \frac{Ryd \ a_o}{h} = 1 \qquad (26)$$

At low enough velocities, and at low enough projectile charges, the method of the perturbed stationary states and the Born approximation, as they both become valid concurrently, gives close results. There is in fact a "compromise" approach which was originally performed by Frame.[18] It involves treating the wavefunction as an atomic wave function perturbed to first order by the projectile.

V.

The remainder of this paper will deal with the
specific problem of K-shell excitation and ionization in
collisions between heavy atoms.

First, it should be pointed out that K-Xrays are
not seen in a collision between two heavy atoms ($Z \tilde{=} 50$) at
energies below a few MeV. Thus, measurements of K-Xrays
from collisions of this type have been performed only very
recently, with high energy apparatus, and are still at an
early stage to this day.

Even at these high energies however, distortion of
the target wave functions is still considerable due to the
high charge of the projectile. More precisely, the universal
velocity obtained from scaling down laboratory velocities
corresponding to energies as high as 100 MeV are quite
small, (less than unity) and if both atoms are heavy, then
high energy models simply do not apply.

Curiously enough, the low energy analysis that fills
the literature does not apply either, because the energy
levels that correspond to the K-shells of heavy atoms do not
cross with those of vacant shells. Whereas energy level
crossing dominates excitation processes in collisions of
light atoms, and in the outer shells of all atoms, most of
the low energy analysis which fills the literature does not

apply to our problem. One might say that this particular problem derives the worst of both worlds.

It is necessary then, to apply the perturbed stationary state method to this situation. The mathematical complexity involved in solving this model can be experienced by considering the wave function of even a simple hydrogen molecule.

Another difficulty involved is not knowing how much of the vacancy production cross-section is due to ionization processes, and how much is due to excitation processes; i.e. how many, if any, of the infinite number of excitation processes is it necessary to consider? And if excitation processes contribute to the cross section considerably, is it in fact necessary to consider ionization? This is still an unsolved problem.

If ionization is to be considered, how does one model the free state wave functions? As a rough start, one might select the free wave functions to be "orthogonalized plane waves," that is, to take a plane wave and subtract from them their ground state component. This method of orthogonalization was employed with some success by Peach[19] in calculation ionization cross-sections for helium. In that situation however, they expand in terms of atomic wave functions, and the free state atomic wave functions before orthogonalization are taken to be the free state solutions in a

central Coulomb field. Here, our Hamiltonian, containing
a two-center Coulomb field potential term, makes it much
more difficult to choose free wave functions. Neverthe-
less, we conjecture that this orthogonalization procedure
gives a reasonable form for the term $\langle\phi_f|\frac{\partial}{\partial t}\phi_i\rangle$.
In the first place, it goes to zero as it should, in the
limits $t\rightarrow\pm\infty$, $v \rightarrow o$. Furthermore, it is directly proport-
ional, as is the true term in real life, to the change of
the ground state wave function with time, so it is reason-
able to expect that at every point in time, this approxi-
mation gives the correct local form for the term $\langle\phi_f|\frac{\partial}{\partial t}\phi_i\rangle$
To shorten the work, one would probably want to use solutions
solved in cylindrical coordinates, (instead of concnical
plane waves) because at any given instant, the Hamiltonian
has cylindrical symmetry.

The molecular wave functions could be approximated
by the conventional LCAO method.

Furthermore, it is possible to do experiments which
can measure vacancy production cross section as a function
of impact parameter.[20] Such experiments in fact have been
performed for the case of L shell vacancy production. This
will make it that much easier to calculate an observable
number. Specifically, one will be able to calculate probab-
ilities for processes at a given impact parameter, (in
particular at very small impact parameters where the analysis
is easier), instead of having to sum over all relevant impact

parameters.

The rest of the paper will be devoted to deriving qualitative features of the results. We can look at the asymptotic behavior of the cross-section curve as a function of velocity, at low and high velocities, i.e. when $\omega\Delta t <<|$ where Δt is the time duration of the collision. The asymptotic limits of v are thus characterized by $v\mathop{\lessgtr}\limits^{<<}_{>>}\Delta x\omega$

Δx = atomic dimension, ω = atomic frequency.

At low velocities, this model is valid, and at asymptotically high velocities, the results are completely meaningless. The motivation for looking at the high velo-city behavior is that it gives us some idea of what the in-between portion of the curve looks like.

As pointed out by Bates and Massey, we can categorize transitions into two categories, those in which the electron changes z-angular momentum and those in which it does not. In the former case, the radial motion of the internuclear distance vector does not contribute to the excitation process and in the latter case, the angular motion of this vector does not contribute to the excitation. These two facts follow from inspection of the symmetries of the situation. Specific-ally, all of the adiabatic solutions have a well defined angular momentum around the internuclear axis. If ϕ_F and ϕ_i have different angular moment about this axis, then the term $<\phi_f|\frac{\partial}{\partial t}\phi_i>$ contains a factor $\int_o^{2\pi}e^{im\phi}d\phi = 2\pi\delta_{om}$ where m is equal to the difference in angular momentum about this axis

between the two states. In the case of σ-σ transition, a
case which includes all transitions from the K-shell to
states with zero angular mementum about the internuclear
axis, $<\phi_f|\frac{\partial}{\partial\theta}|\phi_i>$ is anti-symmetric with respect to η
where θ is the angle between the internuclear axis and any
fixed direction, and η is the angle subtended from the
internuclear axis.

$$\eta \equiv \sphericalangle \ e^- \ AB$$
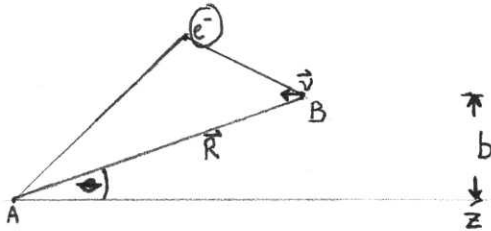
φ is the angle between the plane of the paper and the
plane A e⁻ B.

We now consider the subcases of zero and non-zero
impact parameter colisions. Zero impact parameter we mean
that the impact parameter is small compared to the dimensions
of the ground state atomic wave function.

We will for the time being, neglect changes in the
energy level separation. As we will show later on, all the
arguments we present hold if we use the energy separation at
t=0, and if the energy separation is the same order of magni-
tude at all times.

The term $\langle\psi_f|\frac{\partial}{\partial R}|\psi_i\rangle$ as pointed out by Bates and Massey[9] is anti-symmetric about t=0 (the point of closest approach of the two nuclei). The term $\langle\psi_f|\frac{1}{R}\frac{\partial}{\partial\theta}\psi_i\rangle$ is symmetric about this point. Both these facts follow trivially by inspection.

So we may integrate from 0 to ∞ and use sin( ) and cos( ) functions (instead of exp( )). For the respective processes in which z-angular momentum remains 0, (σ-σ transitions) and where it changes (we refer to all the latter processes as σ-π transitions for convenience).

For the time being, we assume straight line trajectories with of course, constant speeds.

$$\langle\psi_f|\frac{\partial}{\partial z}\psi_i\rangle = \frac{z}{(z^2+b^2)^{1/2}}\langle\psi_f|\frac{\partial}{\partial R}\psi_i\rangle \tag{27}$$

where b is the impact parameter.

The angular contribution to $\langle\psi_f|\frac{\partial}{\partial t}\psi_i\rangle$

is $\frac{\sin\theta(t)}{v}\langle\psi_f|\frac{1}{R(t)}\frac{d}{d\theta}\psi_i\rangle = \frac{b}{v\,R(t)^2}\langle\psi_f|\frac{d}{d\theta}\psi_i\rangle \tag{28}$

σ-σ transitions:

$$a = \int_0^\infty \frac{z}{(z^2+b^2)^{1/2}} \, F(R) \sin \frac{\omega z}{v} \, dz \qquad \text{where } f(R) = \langle \psi_f | \frac{\partial}{\partial R} | \psi_i \rangle$$

$$\equiv \int_0^\infty g(z) \, \sin \frac{\omega z}{v} \, dz \qquad \text{where } g(z) = \frac{z}{(z^2+b^2)^{1/2}} f(\sqrt{z^2+b^2})$$

by successive integrand by parts, we can obtain a power

series in $\frac{v}{wb}$ and $\frac{v}{w} \frac{d}{dz}$ for the transition amplitude.

$$a = \sum_{\substack{\text{odd} \\ n}} \Big|_0^\infty (\frac{v}{\omega})^n \frac{d^n}{dz^n} g(z) \cos \frac{\omega z}{v}$$

$$= \sum_{\substack{\text{odd} \\ n}} (\frac{v}{\omega})^n \left| \frac{d^n}{dz^n} g(z) \right|_{z=0} \tag{30}$$

by inspection

$$\left| \frac{d^n}{dz^n} \left(\frac{z}{\sqrt{z^2+b^2}} \right) \right| = 0 \qquad \text{for even } n \tag{31}$$

and, assuming $\frac{d^n F(R)}{dR^n}$ exists $\forall n$, $\forall R \, 0$,

$$\left| \frac{d^{(n)}}{dz^n} \, f(\sqrt{z^2+b^2}) \right|_{z=0} \qquad \text{is 0 for odd } n \tag{32}$$

$$\frac{d^{(n)}}{dz^n} \, g(z) = \sum_{i=0}^n m(i) \frac{d^{(i)}}{dz^i} \left(\frac{z}{\sqrt{z^2+b^2}} \right) \frac{d^{(n-i)}}{dz^{n-i}} \, f(\sqrt{z^2+b^2}) = 0$$

$$\text{for odd } n \tag{33}$$

so $a(\nu)$ goes to 0 faster than any power of ν.

For σ-π transitions

$$a = \int_o^\infty \frac{b}{R^2} \langle \psi_f | \frac{\partial}{\partial \theta} | \psi_i \rangle \cos \frac{\omega z}{\nu} dz$$

$$= b \int_o^\infty \frac{1}{(z^2+b^2)} f(R) \cos \frac{\omega z}{\nu} dz \qquad \text{where } f(R) = \langle \psi_f(R) | \frac{\partial}{\partial \theta} | \psi_i(R) \rangle$$

$$= b \sum_{\substack{\text{even} \\ n}} (\frac{\nu}{\omega})^n \frac{d^{(n)}}{dz^n} \frac{1}{\sqrt{z^2+b^2}} f(\sqrt{z^2+b^2}) \qquad (34)$$

again,

$$\left| \frac{d^{(n)}}{dz^n} f(\sqrt{z^2+b^2}) \right|_{z=o} = 0 \qquad \text{for odd } n, \qquad (35)$$

$$\left| \frac{d^n}{dz^n} \left(\frac{1}{\sqrt{z^2+b^2}} \right) \right|_{z=o} = 0 \qquad \text{for odd } n, \qquad (36)$$

so

$$\frac{d^{(n)}}{dz^n} \left(\frac{f(\sqrt{z^2+b^2})}{\sqrt{z^2+b^2}} \right) = 0 \qquad \text{for even } n \qquad (37)$$
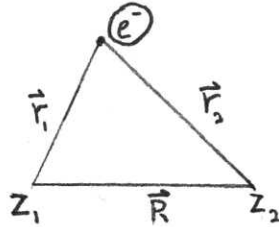
and again $\qquad \frac{a(\nu)}{\nu^n} \underset{\nu \to o}{\to} 0 \qquad \forall n$.

For σ-π transitions, 0 impact parameter collisions do not cause any excitation.

For σ-σ transitions, 0 impact parameter excitation amplitude is given by:

$$a = \int_0^\infty f(R) \sin\frac{\omega z}{v} \, dz \qquad (38)$$

We must now look at $\dfrac{d^{(n)}F(R)}{dR^n}$ more closely. At small R, we treat the finite separations of the nuclei with first order perturbation theory.

$$\psi_i(R) = \sum_n \frac{\psi_n(o)}{E_i - E_n} V'_{in}(R)$$

$$V_{(R,r)} = \frac{z_1 e^2}{|\vec{r}_1|} + \frac{z_2 e^2}{|\vec{r}_2|} = \frac{(z_1)e^2}{|\vec{r}_1|} + \frac{z_2 e^2}{\sqrt{r_1^2 - 2r_1 R \cos + R^2}} \qquad (39)$$

$$V^1 = V - \frac{(z_1 + z_2)e^2}{|\vec{r}_1|} = z_2 e^2 \left(\frac{-1}{r_1} + \frac{1}{\sqrt{r_1^2 - 2r_1 R\cos\phi + R^2}} \right)$$

$$\qquad (40)$$

$$= \frac{z_2 e^2}{r} \left(-1 + \frac{1}{\sqrt{1 - \frac{2R}{r}\cos\phi + \frac{R^2}{r^2}}} \right)$$

$$= \frac{z_2 e^2}{r} \left(\frac{R}{r}\cos\theta - \frac{R^2}{2R^2} + \sum_{mn} C_{nm} \cos\theta^n \left(\frac{R}{r}\right)^{m+2} \right)$$

$$f(o) = \langle \psi_f(o) \mid \frac{\partial}{\partial R} \psi(R) \rangle \bigg|_{R=0} = \tag{41}$$

$$\frac{\partial}{\partial R} \langle \psi_f(o) \mid \psi(R) \rangle \bigg|_{R=0} =$$

$$z_2 e^2 \langle \psi_f(o) \mid \frac{\cos\theta}{r^2} \mid \psi_i(o) \rangle$$

$$a(\nu) = \nu^{-1} z_2 e^2 \langle \psi_f(o) \mid \frac{\cos\theta}{r^2} \mid \psi_i(o) \rangle \tag{42}$$

Here we see that the higher the velocity, the more angular momentum the electron can gain during the collision, as higher derivatives of F come into play, and higher powers of cos θ become involved in the perturbation.

For nuclei of roughly equal sizes, the straight trajectory approximation is, surprisingly enough, equally valid for all atoms. For the dimensionless number $\frac{\Delta v_y}{v_z}$ characterizing the deflection at an impact parameter $\frac{a_o}{10Z}$ equals

$$\tag{43}$$

For a projectile moving at one tenth the orbital velocity of the electron, (remeber $v_z{}^2$ thereby scales as z^2), $\dfrac{\Delta v_y}{v_z} \ll 1$.

Besides the straight trajectory approximation, we see that results scale at any given scattering angle of the projectile, according to the usual scaling scheme.

To summarize, we see that for σ-π type transitions, a→o faster than any power of v. For transitions, at impact parameters (much) greater than $v/_w$, a→0 faster than any power of v and for impact parameters (much) smaller than $v/_w$, $a/_v \to$ constant as v→o. It is important to realize that at small enough velocities, there are no such small impact parameters. The probability of a certain process taking place goes as a^2.

If exact classical trajectories are used for transitions, then

$$\frac{1}{dt} = \frac{1}{dR} \sqrt{\frac{2}{m}(E - \frac{z^2 e^2}{R} - \frac{1^2}{R^2})} \qquad (44)$$

all even derivitives of $\sqrt{\dfrac{2}{m}(E - \dfrac{z^2 e^2}{R} - \dfrac{1^2}{R^2})}$

are 0 at the distance of closest approach.

Hence, $a(\nu) \to 0$ faster than any power of ν, in this case. For 0 impact parameter collisions however, this asymptotic behavior takes over only when the straight trajectory approximation begins to fail.

If the change in ω is taken into account, then the series expansion becomes more complicated

$$a(\sigma-\pi) = \frac{f}{b^2 + z^2} \cos \frac{1}{\nu} \int\omega(z)dz) \quad dz \tag{45}$$

$$= \frac{f}{b^2 + z^2} \cos (\frac{z}{\nu} \Omega(z)) \quad dz$$

where

$$\Omega(z) = \int \frac{\omega (z) dz}{z}$$

without going into too much detail it is clear that

$$\int \begin{array}{c} \cos \\ \sin \end{array} (\frac{\Omega(z)}{\nu} z) \, dz \approx \frac{\nu}{\Omega(z)} \begin{array}{c} \sin \\ \cos \end{array} \frac{\Omega(z)z}{\nu} \tag{46}$$

because

$$\nu\sin(\frac{\Omega(z)z}{\nu}) \frac{d}{dz} (\frac{1}{\Omega(z)}) = \frac{\nu}{\Omega}\sin (\frac{\Omega(z)z}{\nu}) [\frac{d\Omega/dz}{\Omega}]$$

$d\Omega/dz$ is certainly less than $\frac{\Omega}{a}$, where a is the radius of the atomic shell. And $\frac{\nu}{\Omega a} \ll 1$. It is also clear that

$$\frac{d}{dz} \frac{1}{\Omega(\sqrt{z^2+b^2})} \bigg|_{z=o} = 0$$

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So the contribution to the excitation from $\frac{d}{dz}\left(\frac{1}{\Omega}\right)$

could only go as a very high power (≥ 4) of ν as $\nu \to 0$, and

is not worth checking more thoroughly.

For asymptotically high velocities, σ-π transitions

$$a = \int \underbrace{\frac{b}{(z^2+b^2)^{1/2}} \langle \psi_b | \frac{\partial}{\partial\theta} | \psi_a \rangle}_{g(z)} \cos\left(\frac{\int\omega dz}{\nu}\right) \, dz \qquad (46)$$

$$\to \int_0^\infty g(z) \, dz$$

For σ-σ transitions,

$$a = \int_0^\infty \frac{dR}{dz} \, f(R) \, \sin\left(\frac{\int\omega dz}{V}\right) \, dz = \int_0^\infty \frac{dg(\sqrt{z^2+b^2})}{dz} \qquad (47)$$

$$\sin\frac{\omega z}{V} \, dz$$

where

$$g(R) = \int_R^\infty f(r') \, dr'$$

$$a = \frac{1}{\nu} \int_0^\infty g(\sqrt{z^2+b^2}) \, \omega \, \cos\left(\frac{\int\omega dz}{\nu}\right) \, dz \to \frac{1}{\nu}\left(\int_0^\infty g\sqrt{z^2+b^2} \, dz\right.$$

$$(48)$$

We might expect the total cross-section therefore,

to level off and eventually start decreasing at high velo-

cities, according to the perturbed stationary state model.

We now summarize our qualitative knowledge of the entire cross sectional curve as a function of velocity. In a given velocity region, for most impact parameters, if the velocity is low enough, the probability of excitation or ionization will, roughly speaking, behave as a very high power of v. (In fact it will behave as a higher power of v than any power of v.) For very small impact parameters, the probability of excitation will go as v^2. As the velocity gets smaller, the former set of impact parameters becomes more and more dominant. On the other hand, as the velocity is increased, the cross section curve will eventually become concave down as it begins to level off.

So while it is therefore impossible to ascribe a particular power law to the cross-section as a function of energy, there is a local power law at any velocity region for which the power decreases with increasing energy.

The qualitative picture would look something like this:
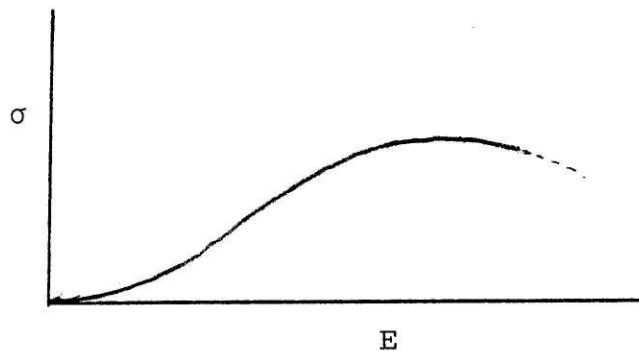
SUMMARY

We see that for heavy projectiles, the Born approximation fails, even for heavy targets, at all velocities except perhaps extreme relativistic velocities. Furthermore, the energy curves corresponding to K-shells of heavy targets do not cross with those of any vacant states; hence the curve-crossing phenomena, which cause cross-sections orders of magnitudes larger than non-resonant mechanisms, would not be expected to apply to K-shell excitation. In fact, recent experiments[1] in heavy ion bombardment have shown that L-shell vacancy production cross-sections are orders of magnitude higher than those of K-shells. Since the K-shell energy curves maintain a large separation between all other curves, the perturbed stationary state method, or some modification thereof, seems appropriate.
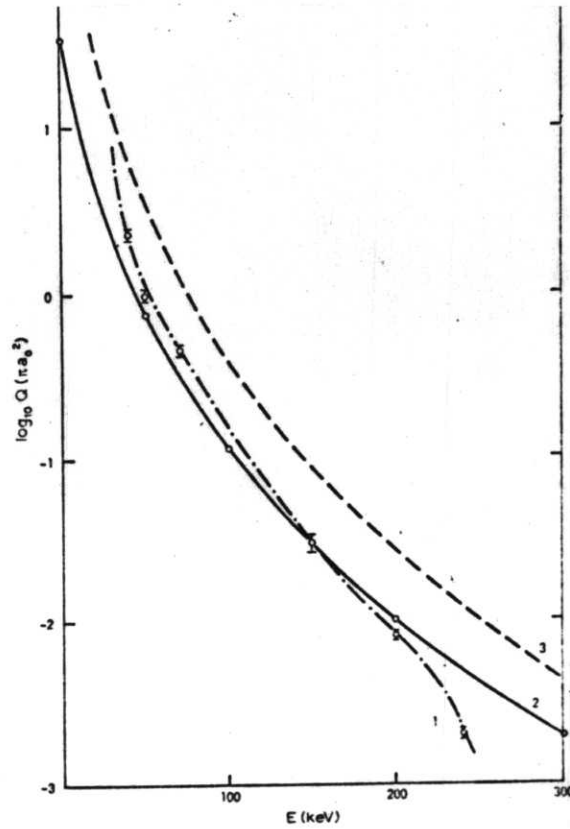
Figure 1. Resonant electron capture. 1)Experiment (Wittkower
et al. (1966)); 2) Two-state approximation (McCarrol (1961));
3) O.B.K. approximation. The process is $H + H^+ \longrightarrow H^+ + H$

(Reprinted from Introduction to the Theory of Ion-Atom Collisions
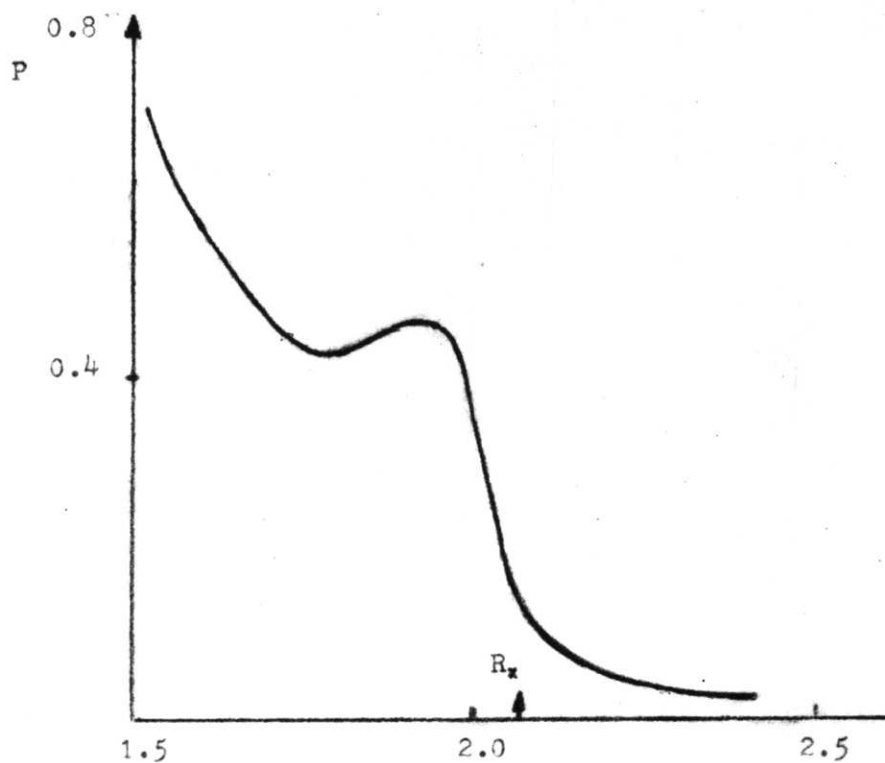by McDowell and Coleman.)

Figure 2. Observed probability of single electron capture
in O + Ne   O + Ne at 2.6 keV as a function of impact
parameter (Alan et al. (1967)). The pseudo-crossing occurs
at R = R$_x$.

Reprinted from Introduction to the Theory of Ion-Atom Collisions
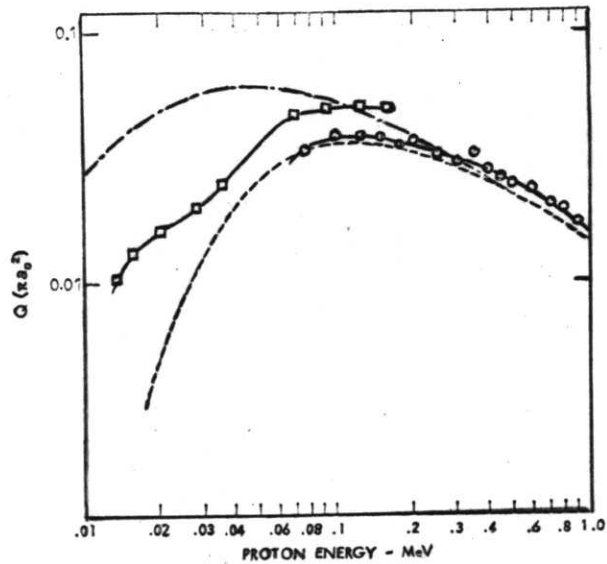by McDowell and Coleman.

Figure 3. Proton impact excitation of He (3p P) ———•——— Theory: Born approximation, Bell (1961); ———————Theory, Distortion approximation, Bell (1961); -□-□- Experiment, De Heer et al. (1968); -o-o- Experiment, Thomas and Bent (1968).

Reprinted from Introduction to the Theory of Ion-Atom Collisions by McDowell and Coleman.
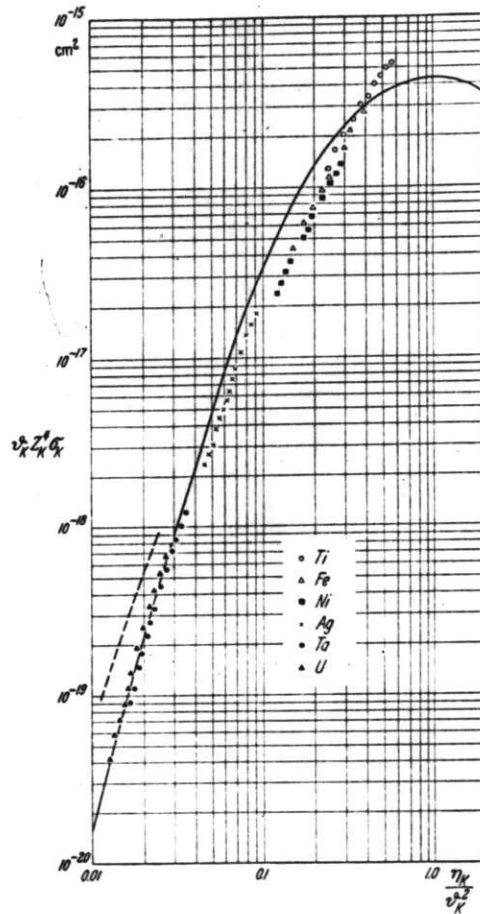
Figure 4 . Composite graph of all K-shell ionization cross
section from proton bombardment at the Duke University
VAN DE GRAAFF accelerator. η_K is the universal parameter
$\frac{1}{2} v^2$. γ_K^2 is a corrective factor due to outer electron
screening.

REFERENCES

1. Schnopper, H.W., et. al (to be published)

2. Specht, H. J., Z. Physik 185, 301 (1965)

3. Kavanagh, T.M., et. al, Phys. Rev. Letters 21, 1731 (1968)

4. Jackson Classical Electrodynanics, (John Wiley & Sons) p. 520

5. B. L. Moiseiwitsch, Proc. Phys. Soc. (1966), Vol. 87, p. 885

6. D. S. F. Crothers and A. R. Holt, Proc. Phys. Soc. (1966) Vol. 88, p. 75

7. Introduction to the Theory of Ion-Atom Collision, McDowell and Coleman, p. 147

8. Zener, C. 1832, Proc. Roy. Soc. (London) A137, 696

9. Bates, D.R., Massey, H.S.W., and Stewart, A.L., (1953) Proc. Roy. Soc. (London) A216, 437

10. Lichten, Phys. Rev., Vol. 164, No. 1, Dec. 1967, p. 131

11. McDowell and Coleman, p. 141

12. Wiluts, L., and Gallaher, D.F. (1966), Phys. Rev. 147, 13

13. Bates, D. R., Proc. Camb. Phil. Soc, 33 (1958) 175

14. Merzbacher and Lewis, Handbuch Der Physic, Vol. XXXIV p. 166

15. McDowell and Coleman, p. 111

16. Bates, D.R. , Proc. Phys. Soc. (London) 73, p.227

17. Henneberg, W., Z. Physik (1933) 86, p.592

18. Frama. Proc. Camb. Phil. Soc. 33 (1937) 115

19. Peach, G. (1965) Proc. Phys. Soc. <u>85</u>, p. 709

20. Stein, H. J. et. al, Phys. Rev. Letters (1970)
     Vol. 24, No. 13, p. 701.