A ONE AND A HALF CENTERED EXPANSION FOR ION-ATOM COLLISIONS[†]

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Fast ion-atom collisions in which charge transfer plays a dominant role have been traditionally treated by a two center expansion (TCE): the state wavefunction is approximated by a truncated set of Hilbert states centered on the target and projectile. This method is accurate but expensive in the use of computer time. We present a new method which allows charge transfer through variational time independent amplitudes, and target excitation and ionization through variational time dependent amplitudes. The method retains the efficiency of a single centered expansion and yet reproduces the conventional TCE results in situations where charge transfer is dominant. Comparison to experiment is made.

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The idea that ion-atom collisions can be efficiently described by a truncated expansion of the state wavefunction ψ_0 in a set of Hilbert functions centered on the target atom e.g., Holt and Moiseiwitsch, 1969 was abandoned as soon as the importance of charge transfer to a complete description of the interaction was realized. This single centered expansion (SCE) was replaced by a two centered expansion (TCE) where two sets of Hilbert functions centered on the target and moving projectile are used. See Shakeshaft, 1978, for an accurate calculation of the proton-hydrogen system and references to earlier literature.

It therefore seemed to demonstrate a certain naivety when the SCE method was reintroduced (Reading et al, 1976) in response to the renewed experimental interest in inner shell ionization spearheaded by Brandt's group (Basbas et al, 1973). There were however several sound reasons for this revision, some to do with physics and some to do with mathematics. In the former class we may cite:

(a) The fact that for asymmetric systems such as protons on copper charge transfer is not at all important to an inner shell process.

(b) The fact to adequately describe ionization a large number (~ 10) of pseudo states must be placed in each (l,m) channel to correctly span the energy range of ejected electrons (Ford et al, 1977).

(c) The fact that antisymmetry considerations (Reading and Ford, 1980) determine that an accurate calculation of multi-hole processes necessitates the simultaneous inclusion of all amplitudes for the

"passive" electrons present in the system as the passive electrons interfere with the primary processes under consideration.

(d) The fact that an overwhelming multiplicity of systems need to be studied as the species and electronic states of the ion and atom are varied.

The last three reasons raise to the point of necessity in any mathematical method used that:

(e) It must include a large number of single particle electronic states, and

(f) it must be practical in the sense of inexpensive to run on a computer.

A last reason for preferring an SCE method over a TCE one is not commonly understood but it is important for the discussion to follow. It is that:

(g) The TCE method is mathematically unsound, because if it is driven to convergence with an increasingly large number of states the over completeness of the two sets of states leads to difficulties:

Points (e) and (f) unfortunately mean that the TCE is out. However point (a) makes a TCE unnecessary hence the revision of the SCE, which with a little numerical ingenuity can be made very efficient in its use of computer time.

For example in Fig. 1 we show a completely first principle calculation of the expected value of inner shell vacancy production as a function of impact parameter produced by a 0.5 Mev proton on copper. The calculation treats the copper atom in a fully non-local Hartree-Fock

model, antisymmetry of the copper electrons is fully taken into account, and the proton is properly slowed down and deflected by the nuclear coulomb repulsion. All of this is done in a few minutes of computing time.

Charge transfer of the electron is of course not explicitly allowed for in the ansatz used to calculate all this,

$$\psi_0^{(SCE)} = \sum_{n=0}^N c_{n0}(t) \chi_n(t). \quad (1)$$

Because $\{\chi_n\}$ is a set of eigenstates formally complete but necessarily in a practical calculation limited to some truncated set,

$$\psi_0^{(SCE)} \rightarrow 0, \quad \text{as } r \rightarrow \infty.$$

Here $\vec{r}$ is the electron coordinate, suppressed in the notation. Thus charge transfer to a projectile eigenstate $\phi_m(t)$ is formally zero because as $t \rightarrow \infty$, $r \rightarrow \infty$ hence

$$\lim_{t \rightarrow \infty} \langle \phi_m | \psi_0^{(SCE)} \rangle \rightarrow 0. \quad (2)$$

This is a simple consequence of the Hilbert nature of $\{\chi_n\}$ and the truncation of the space to $(N+1)$ basis states. Of course if we could let $N \rightarrow \infty$ then Eq. (2) would provide a mechanism for charge transfer as the $\{\chi_n\}$ are complete.

There are two ways out of this if one wishes to calculate charge transfer. The TCE uses two sets of states $\{\chi_n\}$ and $\{\phi_m\}$ in its ansatz for the trial wave function

$$\psi_o(TCE) = \sum_{n=0}^N a_{no}(t) \chi_n(t) + \sum_{m=0}^M b_{mo}(t) \phi_m(t). \quad (3)$$

Now the amplitude for charge transfer is given by $b_{mo}(t_L)$ where t_L is some large time at which we stop integrating the equations of motion.

Another method exploits an idea due to Glauber (1958). He argued in a completely different context that all one ever really needs in a scattering calculation is a good approximation to the wavefunction in the interaction region; because by using a t-matrix integral we have an expression for an amplitude which only necessitates knowledge of ψ_o there, e.g., we could calculate $b_{mo}(t_L)$ by using the expression

$$b_{no}(t_L) = -\frac{i}{\hbar} \int_{-t_L}^{t_L} dt \langle \phi_m | V_T | \psi_o \rangle. \quad (4)$$

Thus a method of calculating charge transfer with SCE is to use $\psi_o(SCE)$ from Eq. (1) in Eq. (4). Of course this idea is not at all unfamiliar. The Brinkman-Kramers, Jackson-Schiff, VPS and Born approximations all use some approximate wavefunction for ψ_o in a t-matrix expression to obtain amplitudes. The difference here is that the accuracy to which $\psi_o(SCE)$ can be pushed is limited only by the extent beyond which it is practical to extend the basis $\{\chi_n\}$. Nevertheless the practical usefulness of such a device has to be demonstrated. It is fair to say that in the many situations tested the SCE method with the employment of Eq. (4) for charge transfer

works well exactly where it would be expected that it should, i.e., in a situation where charge transfer is not dominant.

We illustrate this in Figs. 2-4. In Fig. 2 we plot $\sigma_{\text{C},\text{VK}}^{\text{sf}}$ against energy for protons on carbon. The solid curve is ab initio theory, the experimental points the circles. The cross section for an electron to be captured on to the proton at the same time that a K-shell vacancy is produced in the carbon. In Fig. 3 we plot the cross section for K-shell vacancy production produced by C^{6+} and C^{4+} on argon. The upper curve allows charge transfer and direct ejection of the K-shell electron with the C^{6+} projectile. The lower curve allows only direct ejection as charge transfer to the projectile is suppressed because of the presence of the two electrons on C^{4+} (Reading and Ford, 1980). The solid curve here is the experimental result, the circles are the theory.

In Fig. 4 we give an example of the impact parameter dependence of charge transfer for 700 keV protons incident on neon. The solid curve is our calculation of the K-shell charge transfer probability $P_{\text{CK}}(B)$, where a factor of 2 is included to account for the two K-shell electrons. The experimental points are from the Aarhus group of Pedersen et al. The experiment measures the differential (in projectile scattering angle) cross section for detecting charge transfer in coincidence with a K-shell hole in the target. The differential cross section was converted into an impact parameter dependent probability by Pedersen et al, using the classical connection between impact parameter and scattering angle for scattering of

the projectile by the Thomas-Fermi potential of the neon. The agreement between theory and experiment is quite good. Also shown for comparison is the $\rho_{cK}^{(B)}$ calculated in the OBK approximation, and $\rho_{cK}^{(B)}$ obtained from making a first Born approximation in Eq. (4) by replacing ψ_0 by the unperturbed target K-shell orbital χ_0 . The OBK result has the correct shape, but the first Born is quite poor.

These and many more successes notwithstanding there is a difficulty with the SCE. It does not satisfy unitarity. The probabilities for transitions to the pseudo states $|c_n(t_L)|^2$ already sum to unity and the addition of a number of $|b_{mo}(t_L)|^2$ violates unitarity. Of course this is not serious if b_{mo} is small but some double counting is going on, which may become serious as we move into a region of parameters where charge transfer is important. Further, the method definitely breaks down there. In Fig. 5 $n=2$ excitation of hydrogen by protons is well reproduced above 50 keV by the SCE method but fails below this energy as charge transfer becomes an important channel for electron flux from the target. It turns out that Eq. (4) for charge transfer gives excellent results still, even in this low energy region.

What we want to discuss here is a new "one and a half centered expansion", OHCE which retains the computational efficiency of the SCE and yet has the desirable features of the TCE of respecting unitarity, at least at convergence, and more correctly treating the electron flux loss in the charge transfer channels. The essence of

the idea is to expand not ψ_0 in the set $\{\chi_n\}$ but rather the quantity $\psi_0 - \sum_{n=0}^M b_n(t_k) \phi_n(t)$. In this manner we subtract from ψ_0 just that part of the wavefunction that the truncated set $\{\chi_n\}$ cannot reproduce as time gets large and the projectile and target separate. In fact as no charge transfer has taken place yet at large negative times we use

$$\psi_0(\text{OHCE}) = \sum_{n=0}^N a_n(t) \chi_n(t) + \sum_{m=0}^M b_m(t_L) \beta_m(t) \phi_m(t), \quad (5)$$

where $\beta_m(t)$ is an arbitrary function subject only to the boundary condition that $\beta_m(t_L)=1$, $\beta_m(-t_L)=0$. As a preliminary test of the method we kept only a single channel in the ϕ - space, i.e., the K state of the projectile. We chose $\beta_0(t)$ as a step function at the origin. The results are shown in Figures 5-7. Where the crosses and open circles are the results of the OHCE method and the filled circles and triangles experimental results. The solid curve is the old SCE result. The difference between the two OHCE points is a measure of the lack of convergence of the basis $\{\chi_n\}$ and will be discussed below. The speed of the method is that characterized by the SCE. Overall the improvement over the SCE obtained by the OHCE is encouraging. Much more has to be done in studying its convergence properties but we feel that it offers a convenient extension of the SCE approach so that symmetric ion-atom collisions can be studied as successfully as the asymmetric ones have been.

There are many details about the OHCE which are discussed in our paper submitted to the Journal of Physics. However some explanatory comments may not be out of place here.

A natural question that seems to arise is how can $\beta_m(t)$ be arbitrary when $b_{mo}(t)$ is uniquely fixed by the TCE method? To see why this is the case we invoke point (g). The sets $\{\chi_n\}$ and $\{\phi_m\}$ are linearly dependent. If we increase the sets $\{\chi_n\}$ and $\{\phi_m\}$ indefinitely the TCE method would breakdown as the equations used to determine the $b_{mo}(t)$ become ill conditioned. Thus the TCE cannot in fact determine the $b_{mo}(t)$ at all at convergence. They are indeed arbitrary. However we should not overstate the case. If we used the same finite set $\{\chi_n\}$ and $\{\phi_m\}$ and kept sufficient numerical accuracy so that ill conditioned equations were no problem it must be true that the TCE gives a better answer than the OHCE. This is because in the former both the sets $a_{no}(t)$ and $b_{mo}(t)$ are allowed to vary variationally according to the conditions imposed by

$$\langle \chi_n | (i\hbar \frac{\partial}{\partial t} - H) \psi_0(TCE) \rangle = 0, \quad (6)$$

and

$$\langle \phi_m | (i\hbar \frac{\partial}{\partial t} - H) \psi_0(TCE) \rangle = 0. \quad (7a)$$

In the OHCE we allow only $a_{no}(t)$ to vary according to Eq. (6) but we fix $b_{mo}(t_L)$ by using Eq. (4), or by simple algebra, the condition that

$$\int_{-t_L}^{t_L} dt \langle \phi_m | i\hbar \frac{\partial}{\partial t} - H | \psi(OHCE) \rangle = 0. \quad (7b)$$

However the point is that we would hope to be able to use a much larger set $\{\chi_n\}$ in the OHCE than is practical in the TCE. The results of Figs. 5-7 indicate that this new approach is not without merit even for quite moderate sets. In this example we used 9S, 18P, 27D states in $\{\chi_n\}$ and one in $\{\phi_m\}, \phi_0$.

What about the unitarity that was violated by the SCE? It turns out that the OHCE described above will satisfy unitarity at convergence. Violation of that important condition is not built in as in the SCE. However unitarity is not an imposed condition as it is with the TCE where unitarity is satisfied no matter how small the sets $\{\chi_n\}$ and $\{\phi_m\}$ are. We can impose unitarity in this way if we wish by using the condition

$$\int_{-t_L}^{t_L} dt \beta_m(t) \langle \phi_m | i\hbar \frac{\partial}{\partial t} - H | \psi(OHCE) \rangle = 0 \quad (7c)$$

instead of (7b). In Figs. 5-7 the crosses indicate results obtained using (7b), the open circles using (7c). The proximity of the results gives an estimate of the lack of convergence of the method.

What about other choices of $\beta_m(t)$ other than a step function? It turns out that for technical reasons the choice of $\beta_m(t)$ as a step function at the origin is a very convenient one for us to handle in our computer code. However other choices, perhaps guided by

looking at time dependent perturbation theory, might lead to faster convergence in $\{\chi_n\}$. Our next calculation however will be to increase $\{\chi_n\}$ and $\{\phi_m\}$. Eventually of course we must demonstrate convergence in this manner no matter what choice is used for $\beta_m(t)$.

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FIGURE CAPTIONS

- Fig. 1. Expected value of ionization of K-shell electrons of copper by 0.5 Mev protons as a function of impact parameter. Solid curve ab initio calculation including deflection of projectile. Broken curve: rectilinear trajectory. From Swafford et al, 1977. Data from Andersen et al, 1976.
- Fig. 2. Charge transfer in coincidence with K-shell hole production cross sections $\sigma_{C,YK}^{CP}$ with H^+ projectiles on a carbon atom target in the single particle model. The experimental points are from Rodbro et al, 1979. The open triangles are theoretical points calculated with the K-shell orbital energy shifted to give the experimental K-shell binding energy. From Ford et al, 1980.
- Fig. 3. Cross sections for K-shell vacancy production in Ar by C^{6+} , C^{4+} projectiles. The C^{6+} and C^{4+} projectile K-shell vacancy production cross sections plotted as solid curves are smooth curves through experimental presented by Jawara et al, 1976. The closed circles (to be compared with upper curve) are our calculated K-shell vacancy production cross sections (ionization plus charge transfer), whereas the open circles (to be compared with lower curve) are the K-shell ionization cross sections. The calculations were carried out for a bare C^{6+} projectile, and are from Becker et al, 1980.

Fig. 4. Impact parameter dependence of K-shell charge transfer for 700 keV protons on neon. The solid curve is our coupled-state calculation, the chain curve the OBK, and the dashed curve the result from making a first Born approximation in our t-matrix expression for the charge transfer amplitude (Ford, Reading and Becker, 1980). The experimental points are from the Pederson et al, group at Aarhus.

Fig. 5. Cross section (in units of 10^{-16} cm^2) for $n=2$ excitation in proton-hydrogen collisions. The experimental points (with error bars) are from Park et al, 1975 and 1976. The solid curve is our theoretical single-centered expansion result, and is very similar to that published previously (Fitchard et al, 1977). The crosses and open circles are results from the perturbative and unitary methods, respectively, that are described in the text.

Fig. 6. Cross section (in units of 10^{-16} cm^2) for $n=3$ excitation in proton-hydrogen collisions. The points and curve are as in Fig. 5.

Fig. 7. Cross section (in units of 10^{-16} cm^2) for ionization in proton-hydrogen collisions. The solid curve, crosses, and open circles are the results of our single centered expansion, perturbative, and unitary calculations, respectively, as in Fig. 5. The experimental points (with error bars) are from the following sources: triangles, Park et al, 1977; squares, Fite et al, (1960); circles, Gilbody and Ireland (1963).

Fig 2

Fig:3

Fig. 4

Proton-Hydrogen
n=2 Excitation

X Perturbative
O Unitary
— FFR

Proton-Hydrogen n=3 Excitation

Proton-Hydrogen Ionisation