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Two-Center Thomas-Fermi Model for Adiabatic Ion-Atom Collisions

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We propose a two-center model for the description of ion-atom collisions proceeding via a quasimolecular (adiabatic) mechanism. The electronic potential of the model is given by a superposition of modified *atomic* Thomas-Fermi potentials, each centered about one of the colliding nuclei. Molecular correlation diagrams calculated for the Ne-Ne system show good agreement with results from molecular-orbital Hartree-Fock calculations.

In the past few years the electron-promotion model[1] has proven to be quite successful[2] in describing the excitation of inner-shell electrons in adiabatic ion-atom collisions. Based on the Born-Oppenheimer approximation, the model assumes the formation of a transient quasimolecule whose electronic energy spectrum as a function of the internuclear distance ("correlation diagram") is the starting point for any dynamical treatment of the process. While for a few cases quantitative adiabatic correlation diagrams have been calculated by the Hartree-Fock method,[3,4] the evaluation of most of the experimental results has been based on rather qualitative "diabatic" diagrams. They are obtained from the known electronic spectra in both the united-atom and the separated-atom limits using the correlation diagrams for unscreened Coulomb centers as a guide to connect the limiting cases.[1,5]

It is quite clear that for a more quantitative discussion of experiments and a detailed dynamical theory a method is needed which yields accurate adiabatic correlation diagrams like the Hartree-Fock method and yet is flexible and simple enough to be easily applicable to any given combination of collision partners.

In the present note we propose a model which we believe to meet these requirements. We start from the observation that *atomic* energy levels may, to a good accuracy, be derived from a statistical Thomas-Fermi (TF) model with a universal spherical single-electron potential $V^{\mathrm{TF}}(r)$ (including corrections for self-interaction and exchange effects). Latter[6] has calculated energy levels for a large number of atomic states using potentials of the form (atomic units are used throughout)

$$V^{\mathrm{TF}}(r)=\begin{cases}-\frac{Z}{r}\left\{\Phi(x)+\frac{3\sqrt{2}}{4\pi}\left[\frac{r}{Z}\Phi(x)\right]^{1/2}\right\}, & \text{if } |V^{\mathrm{TF}}(r)|>\frac{1}{r};\\ -r^{-1}, & \text{otherwise.}\end{cases} \tag{1}$$

Here, $x=r/\mu$ with $\mu=0.8853Z^{-1/3}$, and the screening function $\Phi(x)$ is given by the analytic expression

$$\Phi(x)=(1+0.027\,47x^{1/2}+1.243x-0.1486x^{3/2}+0.2302x^{2}+0.007\,298x^{5/2}+0.006\,944x^{3})^{-1}. \tag{2}$$

The corrections for electronic self-interaction and exchange included in the potential (1) have been discussed in detail by Coulson and Sharma.[7] Although the TF approximation cannot compete in accuracy with elaborate atomic Hartree-Fock calculations available today,[8] it should be sufficiently reliable for the treatment of inner-shell electrons relevant to atomic collision processes.

We here assume that the TF method not only gives a resonable description of the potential felt by a single electron in the united-atom and sep-

arated-atom limits, but is also able to account for the mutual screening and polarization of the atoms at finite internuclear distances $2R$. The potential V acting on a single electron at the distance r_1 from the screened nucleus 1 and at the distance r_2 from the screened nucleus 2 might be obtained by solving the TF equation with the appropriate boundary conditions.[9] While it has been shown by Teller[10] that the TF model cannot give rise to molecular binding it still should provide a reasonable approximation for inner-shell electrons whose binding energy by far exceeds molecular dissociation energies.

Instead of attempting a complete numerical solution of the TF equation, we adopt an idea put forward by Hund[11] as early as 1932 which leads to a simple and transparent approximate form of the electronic potential. According to Hund[11] the molecular potential V for a given internuclear distance $2R$ is represented by a sum of two effective (R-dependent) *atomic* TF potentials $V_i^{\text{eff}}(r_i)$ plus a correction term $W(r_1, r_2)$. Subsequently, the functions $V_i^{\text{eff}}(r_i)$ are chosen separately for each value of R in such a way that $W(r_1, r_2)$ is minimized. In the cases considered explicitly by Hund the quantity W has been shown to be negligibly small[11] and thus

$$V = V_1^{\text{eff}}(r_1) + V_2^{\text{eff}}(r_2). \tag{3}$$

We assume this representation of the molecular potential to be approximately valid for any combination of atomic collision partners and all internuclear separations.

Generalizing Hund's *Ansatz* to allow for nonsymmetric systems ($Z_1 \neq Z_2$) and for the inclusion of exchange terms we may write

$$V_i^{\text{eff}}(r_i) = \begin{cases} -\frac{Z_i}{r_i}\left\{\Phi(x_i(R)) + \frac{3\sqrt{2}}{4\pi}\left[r_i f_i(R)\Phi(x_i(R))\right]^{1/2}\right\}, & \text{if } |V_i^{\text{eff}}(r_i)| > \frac{Z_i}{r_i} f_i(R); \\ -\frac{Z_i}{r_i} f_i(R), & \text{otherwise,} \end{cases} \tag{4}$$

where Φ is the screening function defined in Eq. (2). With the abbreviations $\rho_i = r_i/R$, $y_i = (Z_1 + Z_2)/Z_i$ we have

$$x_i(R) = \frac{r_i Z_i^{1/3}}{0.8853} \frac{\lambda^2 + y_i^{1/3}\rho_i^2}{\lambda^2 + \rho_i^2} \tag{5}$$

and

$$f_i(R) = \frac{1}{Z_i} \frac{\lambda^2 + \rho_i^2}{\lambda^2 + y_i \rho_i^2}. \tag{6}$$

The functions (5) and (6) interpolate between the limiting cases and guarantee that the total potential V approaches the correct values for $r_i \to 0, \infty$ (R fixed) and $R \to 0, \infty$ (r_i fixed). The "smoothing parameter" λ^2 has been determined by Hund to be $\lambda^2 = 3$ for the ground states of the N_2 and F_2 molecules. In general, one may expect a dependence of λ^2 on the atomic numbers Z_1 and Z_2.

Having established the potentials (4) acting on the electron, the Hamiltonian of our two-center TF model is expressed by

$$H = -\tfrac{1}{2}\nabla^2 + V_1^{\text{eff}}(r_1) + V_2^{\text{eff}}(r_2). \tag{7}$$

The eigenenergies are obtained by diagonalizing the Hamiltonian (7) in a basis set which has originally been introduced by Hylleraas[12] and recently been used[13] for treating the unscreened relativistic two-center, one-electron problem. It is given by

$$\Psi_{nl}^{m}(\xi, \eta) = (\xi^2 - 1)^{m/2} \exp\left(-\frac{\xi - 1}{2a}\right) L_n^m\left(\frac{\xi - 1}{a}\right) P_l^m(\eta), \tag{8}$$

where $\xi = (r_1 + r_2)/2R$ and $\eta = (r_1 - r_2)/2R$ are prolate spheroidal coordinates and L_n^m and P_l^m are the associated Laguerre polynomials and Legendre functions, respectively. The quantum number m is the (positive) projection of the electronic angular momentum on the internuclear axis, and $n = 0, 1, \ldots, n_{\max}$; $l = m, m+1, \ldots, l_{\max}$ label the matrix elements in our truncated representation. The scaling factor a is connected with the asymptotic behavior of the wave functions and may be adjusted for a given basis set so as to give optimal convergence. It should be mentioned that the set (8) is nonorthogonal with respect to

the labels n and l. For obtaining the eigenvalues one has therefore, to prediagonalize the overlap matrix. In a second step the Hamiltonian (7) is diagonalized in the resulting orthogonal representation. It is clear that for large internuclear separations the basis (8) ceases to be suitable. Then one may use, for example, the combined space of two spherical representations associated with the two nuclei.

As a test on our computer program we have recalculated the well-known energy spectrum of the H_2^+ molecule[14] and achieved an accuracy generally better than 10^{-3} for a wide range of internuclear distances and energies ($2R \leq 20$, principal quantum number $n \leq 5$ with $n_{max}=6$, $l_{max}=m+7$, $a=1/R$).

By way of example we have calculated the adiabatic correlation diagram for the Ne-Ne system (Ne on Ne) shown in Fig. 1. We have chosen this case in order to compare with the Hartree-Fock

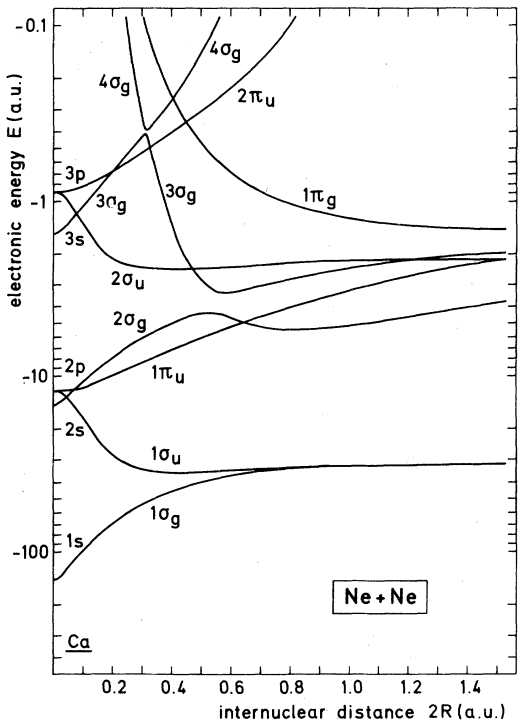

FIG. 1. Correlation diagram for the Ne-Ne system, calculated from the Hamiltonian (7). The calculation has been restricted to $\sigma(m=0)$ and $\pi(m=1)$ states; the levels are labelled according to their "gerade" (g) or "ungerade" (u) character. The parameter values used in the calculation are $\lambda^2=3$, $a=1/10R$, $n_{max}=6$, $l_{max}=m+7$. At $R=0$, the electronic energies have been determined directly by solving the radial Schrödinger equation with the united-atom TF potential.

calculations of Larkins.[3] In fact, it turns out that we are able to reproduce the results of those detailed calculations with a remarkable degree of accuracy. An avoided crossing $3\sigma_g$-$4\sigma_g$ is found at $2R=0.31$, $E=-0.40$ with a closest separation of $\Delta E=0.01$.

It should be pointed out that in the absence of a screening potential the *avoided* crossings would turn into *real* crossings due to the existence of an additional symmetry for the two-center Coulomb problem.[15] The resulting correlation diagrams are usually called *diabatic* diagrams. Since the closest separation of electronic energy levels near avoided crossings is a direct measure of the deviation from a two-center Coulomb potential (screening), possible experimental information on such separations may, conversely, be used to test and correct the theoretically assumed screening.

In conclusion we wish to summarize what we believe are the main advantages of the proposed two-center TF model: (i) The model gives a conceptually very simple picture which might serve as a basis for the discussion of adiabatic ion-atom collisions. (ii) Comparisons with existing Hartree-Fock calculations indicate that the model gives quantitatively reliable results. (iii) While for heavier systems complete two-center Hartree-Fock calculations are hardly feasible, the numerical effort required by our model is independent of the number of electrons in the system. We may therefore calculate adiabatic correlation diagrams for systems which hitherto have been inaccessible. (iv) Because of the simplicity of obtaining energy levels and one-electron wave functions (which possibly may *not* have the same quality as the energies) our model may serve as a suitable starting point for calculations on the collision dynamics. As a first extension we intend to investigate, in the framework of a modified TF approximation, the effect on correlation diagrams caused by outer-shell ionization and by inner-shell vacancies.

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Mechanisms for Electron Production in 30-MeV $O^{n+}+O_2$ Collisions*

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Absolute cross sections for electron emission in the complete energy and angular ranges were measured for 30-MeV $O^{n+}+O_2$ collisions at incident charge states of $n=4$ to 8. Rises in inner- and outer-shell ionization of the target are studied for increasing n. Electrons ejected from the outer shell of the projectile are found to be very intense at forward emission angles θ. Auger electrons from the projectile are observed at $\theta < 42°$ for n as large as 6.

Most previous measurements of electron production in ion-atom collisions have been made with projectile energies lower than a few MeV; for recent progress in this field see current reviews.[1,2] Only recently, Burch and co-workers[3-5] and Matthews and co-workers[6] using ions from tandem Van de Graaff accelerators reported on electron production in experiments with projectiles having energies an order of magnitude higher than previously used. In these experiments, however, electrons have been measured only at fixed backward angles with respect to the incident beam, and only certain fractions of the electron spectra (target Auger peak[3,5,6] and projectile "electron-loss" peak[4]) have been detected. Our purpose in this work is to study the overall angular and energy distributions of secondary electrons produced by energetic heavy ions with a variety of incident charge states. This is the first such comprehensive investigation for high-energy collisions and it is made to obtain a general picture of ionization mechanisms with ions supplied from high-energy accelerators.

We report absolute cross sections for electrons ejected in 30-MeV $O^{n+}+O_2$ collisions with projectile charge states of n from 4 to 8. Measurements were made at forward observation angles of 25 to 90°; the data do not substantially change in the range of backward angles. The measured electron spectra indicate pronounced structures, each of which can be attributed to certain excitation and de-excitation processes in the target or the projectile atom. It is found that most of the spectral structures are strong only at forward electron-ejection angles. In particular, at small angles outer-shell electrons emitted from the projectile are found to dominate the electron spectra. Furthermore, Auger electrons ejected from the 30-MeV projectile can be observed only at angles smaller than 42°. At 25°, projectile Auger electrons are found for projectile charge states as high as 6, indicating the presence of collision processes such as simultaneous vacancy creation in the inner shell and transfer of two electrons to