Reconciliation of atomic- and molecular-orbital models in slow and symmetric collisions

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A detailed procedure with mostly analytical formulas is given for calculation of the K-shell direct-ionization probabilities in symmetric collisions. This method, based on the Briggs united-atom model, applies in the slow-collision limit. The binding energy is deduced from *a priori* calculations, with averaging over impact parameters done by iteration. Two important effects are included for the first time and are consequences of the molecular-orbital (electron-promotion) model. One is outer-shell excitation that has a significant effect, in addition to ionization, on the binding energy. The other is the anisotropy of the $2p\sigma$ united-atom orbital. After inclusion of the probability of rotational-coupling excitation from the $2p\sigma$ molecular orbital, the predictions agree with the experimental K-shell excitation probabilities of Schuch *et al.* for Ni-Ni collisions at 54.4 MeV. Thus, united- and separated-atom calculations are reconciled within the common framework of the molecular-orbital model and the Born approximation.

I. INTRODUCTION

Madison and Merzbacher[1] outlined schematically regions of validity of the separated-atom (SA) and molecular-orbital (MO) theories for atomic collisions in the Z_1/Z_2 versus v_1/v_K plane, where Z_1/Z_2 was the ratio of the projectile and target atomic numbers and v_1/v_K was the collision velocity in units of the innermost K-shell electron. In Fig. 1, we reproduce these regions by the areas within the solid boundary curves. This famous diagram (see Fig. 13 of Ref. 1) emphasizes the difference between the collision regimes in which these two approaches are applicable. The SA approach considers the collision as a perturbation of the atomic target by the incoming projectile. In first Born approximations, such as the standard plane-wave Born approximation (PWBA) or, equivalent to it, the straight-line semiclassical approximation (SCA), the perturbation treatment becomes increasingly inoperative with decreasing collision velocity (for $v_1/v_K \cong 1$ and below) unless the Z_1/Z_2 ratio drops significantly below 0.1; the validity of the SA approach in the first Born version becomes restricted to progressively more asymmetric collisions in the slow-collision regime. On the other hand, slow and symmetric, or nearly symmetric, collisions are in the domain of applicability of the MO model, which takes into account the mutual distortion in the atomic orbitals of the collision partners. A wide area between the islands of validity of these two apparently different approaches can be appreciably narrowed through an extension (with broken boundary lines) of the perturbative treatment in the SA approach beyond the first Born approximation. This has been in fact achieved in a perturbed-stationary-state (PSS) analysis of the target electron.[2] In the general spirit of the prototype figure from Ref. 1, the dashed curves delineate schematically the upper limit of Z_1/Z_2 for which the PSS approach is expected and found to be valid.[3] In a similar fashion, one envisions the broadening of the area reserved for the MO treatment once molecular orbitals are also subjected to higher-order perturbations.[4]

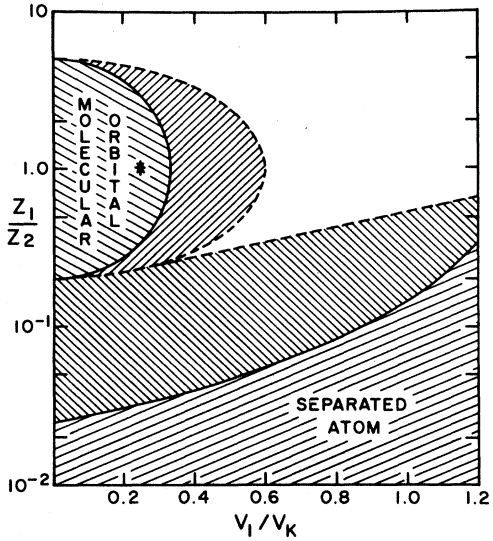

FIG. 1. Regions of validity of first Born approximations in the molecular-orbital (MO) and separated-atom (SA) treatments are enclosed by the solid curves (after Fig. 13 of Ref. 1). The areas delimited by the dashed curves cover the regions of validity of the treatments that extend beyond the first Born approximation. The asterisk at $v_1/v_K = 0.22$ and $Z_1/Z_2 = 1$ shows the datum analyzed in this work using the united-atom (UA) approach.

Nevertheless, a perturbative theory becomes inadequate when applied to the separated target atom in the presence

of a very slow projectile with the comparable atomic number, i.e., precisely in the collision regime where MO models reign.[4] These models consider excitation as a process in which SA orbitals of both collision partners make an adiabatic transition to united-atom (UA) orbitals of higher principal quantum numbers in accordance with the correlation rules of the MO theory. The problem of K-shell excitation is par excellence, as far as elegant interpretation is concerned; the lack of subshells simplifies the theoretical interpretation of experiments. This problem was solved by Briggs and Macek,[5] who restricted themselves to the rotational coupling between $2p\sigma$ and $2p\pi$ states as the mechanism of K-shell excitation. The cross sections found by this method agreed remarkably with the experiments at low projectile velocity and, as delineated by the Madison and Merzbacher diagram, disagreed with the data of higher velocities.

Yet the rotational-coupling calculations failed the more stringent test of comparison with the experimental impact-parameter dependent K-shell excitation probabilities, P_K. As a wealth of data primarily from the group of Schmidt-Böcking and his co-workers[6] was published, the pronounced peaks of the so-called kinematic and dynamic origins predicted in the rotational-coupling model could be barely deciphered in these experiments.

Meyerhof[7] and others[6,8] recognized that the filling of the valley between the rotational-coupling peaks may be due to the K-shell excitation processes other than just the $2p\sigma$-$2p\pi$ transition. Direct ionization to the continuum has been singled out as a main culprit. Meyerhof, following his earlier treatment of the $3d\sigma$ direct ionization,[9] reported[7] the results of direct-ionization calculations for the $2p\sigma$ state and obtained qualitative agreement with the data once the contributions of both rotational coupling and direct ionization were added.

In this paper we implement these ideas quantitatively with a detailed recipe for a consideration of the direct K-shell ionization probability in the molecular-orbital regime. For simplicity we restrict ourselves to symmetric collisions in which the projectile and target atomic numbers are identical, $Z_1=Z_2$.

II. DIRECT IONIZATION IN THE UNITED-ATOM MODEL

A. Ionization probability in the united-atom limit

Let $P(b,v_1)\equiv|a(b,v_1)|^2$ be the impact-parameter b-dependent probability (or differential cross section) such that $2\pi\int_0^\infty P(b,v_1)b\,db=\sigma(v_1)$ with $a(b,v_1)$ being the properly normalized transition amplitude and σ the cross section for a given process due to a projectile of speed v_1. Briggs established[10] the connection between P, the probability for promotion from a molecular orbital and $a^{\rm UA}$, the transition amplitude from the corresponding united-atom orbital with $Z=2Z_1=2Z_2$. It follows from Eq. (9) of Ref. 10 that in the straight-line approximation the cross section for direct ionization in the united-atom (UA) model is

$$\sigma=2\pi\times4\int_0^\infty |a^{\rm UA}(\tfrac{1}{2}b,\tfrac{1}{2}v_1)|^2 b\,db\ . \tag{1}$$

With the change of the dummy variable of integration $b\rightarrow b'=b/2$, σ of Eq. (1) becomes

$$\sigma=2\pi\times16\int_0^\infty |a^{\rm UA}(b',\tfrac{1}{2}v_1)|^2 b'db' \tag{2}$$

so that, with $P^{\rm UA}(b,\frac{1}{2}v_1)\equiv|a^{\rm UA}(b,\frac{1}{2}v_1)|^2$,

$$P(b,v_1)=16P^{\rm UA}(b,\tfrac{1}{2}v_1) \tag{3}$$

instead of $P=4P^{\rm UA}(b,\frac{1}{2}v_1)$ as Eq. (10) of Ref. 10 has it. Equation (2) leads immediately to $\sigma=16\sigma^{\rm UA}(\frac{1}{2}v_1)$ in agreement with the symmetric case of the general formula derived by Zoran *et al.*[11] from the Briggs's UA model.[10]

Thus to calculate the K-shell ionization probability one needs to know $P_{1s}^{\rm UA}$ and $P_{2p}^{\rm UA}$ at $\frac{1}{2}v_1$ and multiply each by a factor of 16. One-half of the laboratory speed of the projectile can be interpreted as its center-of-mass speed in a symmetric collision. The multiplicative factor of 16 can be traced to the square of the two coherently added, identical amplitudes, each twice as large because of replacement of Z_1 in $a^{\rm UA}$ by $2Z_1$. There is no transparent connection between P and $a^{\rm UA}$ for asymmetric collisions; when $Z_1\neq Z_2$, P cannot be expressed in terms of scaled $P^{\rm UA}$ because of a coherent addition of unequal amplitudes. The united-atom model has to be evaluated numerically.[12]

In symmetric collisions the $P^{\rm UA}$ are the separated-atom probability functions with Z_2 replaced by $2Z_2$. These probabilities were numerically calculated in the semiclassical approximation and reported in tabular form by Hansteen *et al.*[13] The tabular values of $P^{\rm UA}$ do not extend to the low-velocity regime ($v_1/v_K<0.15$) and list, at most, only one or two values at the impact parameters smaller than the b at which $P(b)b$ attains a maximum. The tabular P's correspond to large impact parameters at which probabilities for direct K-shell ionization are negligible compared with the rotational-coupling mechanism. The paragraphs that follow remedy this shortcoming.

The concept of the united-atom model applies only in the slow-collision regime with $v_1/v_K\ll1$. Fortunately, in this limit, the leading terms that contribute to P can be identified explicitly as[14]

$$P_{1s}=\sigma_{1s}q_{1s}^2\frac{45x^7}{64\pi}\int_x^\infty\frac{K_2^2(y)dy}{y^4} \tag{4}$$

and

$$P_{2p}=\sigma_{2p}q_{2p}^2\frac{11x^9}{384\pi}\int_x^\infty\frac{[K_2^2(y)+K_3^2(y)]dy}{y^4}\ , \tag{5}$$

where $x\equiv bq_S$ with $q_S=\Delta E_S/v_1$ being the approximate minimum momentum transfer in terms of ΔE_S, the minimum energy transfer in the ionization from the $S=1s$, $2p$ shell, i.e., its binding energy. K_2 and K_3 are the modified Bessel functions of the second and third order. Within 1% convenient analytical approximations to Eqs. (4) and (5) are found as

$$P_{1s}=\sigma_{1s}q_{1s}^2\frac{45}{112\pi}\left[1+1.96x+\frac{7\pi}{16}x^2\right]e^{-2x} \tag{6}$$

and

$$P_{2p}=\sigma_{2p}q_{2p}^2\frac{11}{54\pi}\left[1+2x+1.44x^2+x^3+\frac{9\pi}{128}x^4\right]e^{-2x}\ . \tag{7}$$

To compare these probabilities in magnitude one observes that, in terms of the radii of the $1s$ and $2p$ states, $a_{1s}=1/Z_{1s}$ and $a_{2p}=4/Z_{2p}$, the cross sections are

$$\sigma_{1s}=8\pi a_{1s}^2(Z_1/Z_{1s})^2F_{1s}/\theta_{1s}\ ,$$
$$\sigma_{2p}=32\pi a_{2p}^2(Z_1/Z_{2p})^2F_{2p}/\theta_{2p}\ , \tag{8}$$

where the F_S functions are known analytically[15] and the θ_S's represent the observed binding energies scaled by their hydrogenic values. Based on Eqs. (6)—(8) and the simplifying assumptions that $Z_{1s}\approx Z_{2p}$ and $\theta_{1s}\approx\theta_{2p}\approx 1$, one finds that $P_{2p}/P_{1s}\approx(500v_1/v_K)^2$; thus, even at the slowest collisions observed experimentally, P_{1s} is only about 0.1% of P_{2p}.

B. Direct ionization of the $2p\sigma$ state and anisotropy effects

According to the well-known correlation diagrams[4] direct ionization of K-shell electrons proceeds via removal from the $1s\sigma$ and $2p\sigma$ orbitals of the united atom. Hence, by Eq. (3), K-shell excitation due to direct ionization should be correctly evaluated as

$$P_K^{\rm DI}=16[P_{1s}^{\rm UA}(b,\tfrac{1}{2}v_1)+P_{2p\sigma}^{\rm UA}(b,\tfrac{1}{2}v_1)]\ , \tag{9}$$

where $P_{2p\sigma}^{\rm UA}$ is the probability of ionization of the $2p$ electrons with the magnetic quantum number $m=0$. Meyerhof[7] divided P_{2p} by a factor of 3 on the premise that the collision thoroughly mixed the magnetic substates. This, however, is completely contrary to the assumption of weak coupling which is implied by the perturbative method of calculating the probabilities. Therefore we do not adopt his idea.

Since published tables[13,16] do not apply here, we calculate the directional anisotropy directly. We again take advantage of the slow-collision limit. Tracing the derivation of $P_{2p\sigma}$ to the formulas of Refs. 17 and 18, we find that the $m=0$ state gives in the $v_1/v_K\ll 1$ limit

$$p_{2p\sigma}=\sigma_{2p}q_{2p}^2\frac{11x^9}{384\pi}\int_x^\infty\frac{K_3^2(y)dy}{y^4}\ . \tag{10}$$

An analytical approximation to $P_{2p\sigma}$ can be easily obtained from the already given approximations to P_{1s} and P_{2p} of Eqs. (6) and (7) since

$$P_{2p\sigma}=P_{2p}-(\sigma_{2p}q_{2p}^2/\sigma_{1s}q_{1s}^2)x_{2p}^2P_{1s}(x_{2p})\ .$$

One gets

$$P_{2p\sigma}=\sigma_{2p}q_{2p}^2\frac{11}{54\pi}\left[1+2x+1.36x^2+0.84x^3+\frac{9\pi}{256}x^4\right]e^{-2x}\ . \tag{11}$$

It is interesting to observe that in the low-velocity limit $2\pi\int_0^\infty P_{2p\sigma}b\,db=0.855\sigma_{2p}$, i.e., $\sigma_{2p\sigma}$ is 86%, and not just $\frac{1}{3}$, of the cross section due to all $2p$ electrons. In fact, in this low collision velocity limit $P_{2p\sigma}$ equals $P_{2p\pi}$ ($m=+1$ and -1) at large impact parameters and dominates over $P_{2p\pi}$ at small impact parameters where $P_{2p\pi}=x_{2p}^2P_{2p\sigma}$ as $x_{2p}\to 0$. Thus, depending on the impact parameter, the anisotropy factor varies from $\frac{1}{2}$ to 1 rather than being a constant, statistical factor of $\frac{1}{3}$ as used by Meyerhof.

C. Binding energy in the united and separated collision systems

The most crucial variable in the calculation of direct-ionization cross sections is the binding energy ΔE_S, of the electron ($2p\sigma$ in this case) to be ionized. This is particularly true in the low-velocity limit, where σ_{2p} is inversely proportional to the eleventh power of ΔE_{2p}. Hence, with $P_{2p}\propto\sigma_{2p}q_{2p}^2$ [for example, see Eq. (11)] and $q_{2p}\propto\Delta E_{2p}$, $P_{2p}\propto(\Delta E_{2p})^{-9}$; a 10% error in the binding energy causes a factor of 2 change in the calculated ionization probabilities, as noted by Moar *et al.*[6]

The observed binding energy for a neutral united atom of atomic number $Z=2Z_1=2Z_2$ is, by definition, that value at zero internuclear distance. We modify this inner-shell electron energy by (i) an energy shift due to the removal and promotion of outermost electrons, (ii) a self-consistent extension to finite internuclear distances based on known molecular-orbital eigenenergies.

The energy shift due to loss of the outer electrons is estimated in a simple electrostatic model. For the purposes of the present discussion the total energy is proportional to the electrostatic potential energy; from the virial theorem the total energy for a system of electrons is $\frac{1}{2}$ of its potential energy. In the manner of a classical electrostatic energy calculation, and with the binding energy being the change in total energy upon removal of one electron, the calculation of the binding energy amounts to finding the difference between energies of two classical electrostatic distributions, in which the transfer of one electron makes the difference.

Consider an atom with an inner core of electrons surrounded by spherically symmetric outer shells. The shells are indeed symmetric when closed. From classical electrostatics the potential inside a closed, spherical shell is constant. Thus the change in the electric charge in the outer shells merely shifts all the energy levels of the core electrons by a constant amount. This leads to a simple method of determining the electronic energy levels of a stripped ion core without outer electrons.

Tables of ionization potentials, such as those of Carlson *et al.*,[19] give the binding energy of the outermost electron. The binding energy of any other electron in the core ($2p$ in the present case) is found immediately from the difference in binding energies for various configurations, as reported in Ref. 20, for example. Such a procedure is rigorous only for closed shells. Since the atomic collisions are fast on the scale of outer-electron velocities, and therefore average over all configurations, we find this procedure justified also in the case of open shells.

Table I lists binding energies for the $2p$ shell of $_{56}$Ba, the united atom in a $_{28}$Ni-$_{28}$Ni collision. We estimate the $2p$ binding energy in the 54.4-MeV Ni-Ni collision, for

TABLE I. $2p$ binding energy in $_{56}Ba^{+q}$ ions.

No. of electrons Removed q	Present $Z-q$	Configuration	Binding energy in keV $2p_{av}$
0	56	$(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^6\,(3d)^{10}\,(4s)^2\,(4p)^6\,(4d)^{10}\,(5s)^2\,(5p)^6\,(6s)^2$	5.372
10	46	$(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^6\,(3d)^{10}\,(4s)^2\,(4p)^6\,(4d)^{10}$	5.505
20	36	$(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^6\,(3d)^{10}\,(4s)^2\,(4p)^6$	5.857
28	28	$(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^6\,(3d)^{10}$	6.168
38	18	$(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^6$	7.117
46	10	$(1s)^2\,(2s)^2\,(2p)^6$	7.991
51	5	$(1s)^2\,(2s)^2\;2p$	9.392
55	1	$2p$	10.667[a]
41	15	$(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^3$	7.396[b]
20	36	$(1s)^2\,(2s,2p)^8\,(3s,3p)^5\,(3d)^6\,(4s,p)^2\,(4d)^3\,(4f)^5\;5p\;5f\;(5g)^2\;5h$	6.3[c,d]
			6.5±0.2[e]

[a]Exact nonrelativistic hydrogenic result.
[b]21 electrons removed from Ba^{+20}.
[c]Ba^{+20} with 21 electrons promoted.
[d]Estimated from Slater's screening rules.
[e]Same as *d*, with 55% of $2p$ electrons removed from SA and after some *M*-shell excitation (final estimate for UA $2p\sigma$ binding energy).

which P_K has been measured by Schuch *et al.*[6]

Our basic method to estimate the $2p$ binding energy in the highly excited united atom is to use the total excitation energy of the promoted electrons as a parameter. Based on the equilibrium charge of a 54.4-MeV Ni ion in a Ni foil [see Fig. 5(b) of Ref. 21], we view the collision as a 20 times ionized projectile $_{28}Ni^{+20}$ in the $(1s)^2(2s,2p)^6$ state colliding with a ground-state Ni atom. In the electron-promotion model (see Fig. 4 of Ref. 4), the united atom $_{56}Ba^{+20}$ has a typical configuration as specified in Table II. From Table I, Ba^{+20} in its ground state has a $2p$ binding energy of 5.857 keV. With the additional removal of 21 electrons, Ba^{+41} has a $2p$ binding energy of 7.396 keV. The energy spent to remove these electrons is 35.1 keV.

We estimate that the promotion of the 21 electrons requires 11.5 keV. In this estimate, the binding energy is calculated according to the Mosley expression as $\frac{1}{2}(Z_s/n)^2$, where $Z_s=Z-s$ is the nuclear charge diminished by the Slater's screening constant and n is the principal quantum number. In accordance with our basic method, the correction of the $2p$ binding energy is proportional to the change in the total binding energy of the atom. Interpolating between the values for 20 and 41 missing electrons we obtain 6.3 keV for the $2p$ binding energy in the united atom Ba^{+20} with 21 promoted electrons. As seen in Fig. 2, electron promotion is approximately equivalent to total removal of half of the promoted electrons.

In addition to electron promotion, vacancies and/or excitation, which are caused by nuclear motion, also modify the binding energy of the $2p$ electrons. Information about these processes is very incomplete. From the curve given by Greenberg *et al.*,[22] and correcting for direct excitation,

TABLE II. Effect of electron promotion in Ni^{+20}—Ni collisions. Populations in separated- and united-atom orbitals, with effective nuclear charge $(Z-s)$ for outer shells.

	Separated atom		United atom $(Z=56)$		
	$_{28}Ni$	$_{28}Ni^{+20}$	$_{56}Ba^{+20}$	$(Z-s)$	Remarks
$1s$	2	2	2		CORE
$2s,2p$	8	6	8		
$3s,3p$	8	0	5		
$3d$	8	0	6	41	OUTER
$4s,4p$	2	0	2	35.5	SHELLS
$4d$	0	0	3	33	
$4f$	0	0	4	29	
$5s,5p$	0	0	1	26.5	
$5f$	0	0	1	25	
$5g$	0	0	3	23.3	
$5h$	0	0	1	21	

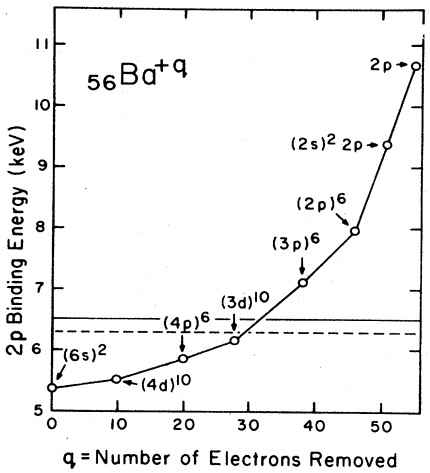

FIG. 2. $2p$ binding energy as a function of ionic charge q; i.e., the number of electrons removed for a $_{56}Ba^{+q}$ ion. The circles, identified by the outermost filled shell, are from our estimates for configurations listed in Table I. The dashed line is the estimated energy level for $_{56}Ba^{+20}$ with 21 promoted electrons. This binding energy is represented by the solid line at 6.5 keV, after a 55% vacant L-shell and M-shell excitations are also assumed.

we deduce that there are 0.55 vacancies in the L shell during a 54.4 -MeV Ni-Ni collision. This means an additional excitation of 2.3 keV, which changes the $2p$ binding energy to 6.4 keV. Other excitations, such as direct M-shell ionization, are expected to alter this value by a lesser amount. We thus finally estimate the binding energy of the $2p$ state to be 6.5 ± 0.2 keV at the zero internuclear distance. Note that an error of 0.2 keV corresponds to a 3% uncertainty in the binding energy. The innermost $1s$ state is thought to be essentially unchanged with the stripping of outer electrons, and, hence, its united, neutral atom observed energy of 37.4 keV is used in our calculations.

The extension of the united $_{56}Ba$ eigenenergies for its molecular orbitals at finite internuclear distance R presents the greatest ambiguity. Although the molecular-orbital diagrams for $1s$ and $2p\sigma$ levels in a Ni-Ni system exist,[23] it is not clear what $\Delta E_S(R)$ one should enter via q_S and σ_S in the evaluation of P_{1s} and $P_{2p\sigma}$. Meyerhof[7,9] approximated $\Delta E_S(R)$ with a parabola at small R and used Hansteen's P functions. Aside from assigning too much weight to small impact parameters by such a procedure, the use of an R-dependent ΔE_S is inconsistent with any calculation of semiclassical ionization probabilities which assumes constant ΔE_S over all internuclear distances.

In our procedure we first renormalize the calculated[23] $\Delta E_S(R)$ to $\Delta E_S^{\rm obs}(R)$ such that

$$\Delta E_S^{\rm obs}(R)=\Delta E_S(R)\,\Delta E_S^{\rm obs}(0)/\Delta E_S(0)\ , \tag{12}$$

where $\Delta E_S^{\rm obs}(0)$ are the observed binding energies in the united $_{56}Ba^{+20}$ taken to be $\Delta E_{1s}^{\rm obs}(0)=37.4$ keV and $\Delta E_{2p}^{\rm obs}(0)=6.5$ keV as explained previously. Equation (12) provides one with the impact-parameter dependent $\Delta E^{\rm obs}(R)$ through the relation of R to b: $R=d+\sqrt{d^2+b^2}$, with $d\equiv Z_1Z_2/Av_1^2$, where $A=(A_1^{-1}+A_2^{-1})^{-1}$ is the reduced mass of the colliding system in electron mass units. An impact-parameter independent ΔE_S is necessary to make use of P_{1s} and $P_{2p\sigma}$, since these probabilities are defined so that σ_S and q_S are independent of impact parameter b, in order to integrate probabilities over all impact parameters to the cross sections σ_S.

To achieve this goal we evaluate the binding energy as a mean over all impact parameters,

$$\langle\Delta E_S\rangle=2\pi\int_0^\infty \Delta E_S(R)P_S^{\rm UA}(b)b\,db/\sigma_S\ .$$

$\langle\Delta E_S\rangle$ is calculated in an iterative manner, starting with $\Delta E_S^{\rm obs}(0)$ in the $P_S^{\rm UA}$ and σ_S. In the next iteration $\langle\Delta E_S\rangle$ is used instead of $\Delta E^{\rm obs}(0)$, a new value of $\langle\Delta E_S\rangle$ is determined, and the iteration is continued. After a few such iterations the successive values of $\langle\Delta E_S\rangle$ are found to converge quickly to a *constant* $\langle\Delta E_S\rangle$.

D. Energy-loss, Coulomb-deflection, and relativistic corrections

Energy-loss, Coulomb-deflection, and relativistic effects can be important in the slow-collision regime.[24] We account for these effects according to the formulas of the ECPSSR theory.[25]

III. COMPARISON WITH EXPERIMENT

To illustrate our procedure for calculation of $P_K^{\rm DI}$, the K-shell direct-ionization probability, we analyze the experiment of Schuch *et al.*[6,26] with 54.4-MeV Ni-Ni. We have chosen a Ni-Ni collision simply because a good (easily readable for our purposes) molecular energy-level diagram exists[23] for this system; we have chosen the 54.4-MeV data because they correspond to sufficiently slow $(v_1/v_K=0.22)$ collision to justify the use of the united-atom model. See the asterisk in Fig. 1.

The data are shown in Fig. 3. The results of our calculations according to the procedures outlined in Sec. II are represented by the dashed curve in this figure. It is worth noting that the energy loss had no practical effect on this curve since $\langle\Delta E_S\rangle/E_1=6.8$ keV/54 400 keV$\cong10^{-4}\ll1$ in the analyzed collision system. The Coulomb-deflection and relativistic effects moved the curve in opposite directions; while the Coulomb-deflection factor lowered it to 0.93 of its straight-line value, the relativistic effect raised it by a factor of 1.26. Also, in accordance with the general estimate made in Sec. IIA, P_{1s} contributes negligibly to direct K-shell ionization for the data considered here.

Our calculations for direct K-shell ionization account only partially for the observed data; the calculated $\sigma_K^{\rm DI}=12$ kb as contrasted with the experimental value of 31 kb.[6,26] The rotational-coupling mechanism which was originally involved to explain $P_K^{\rm expt}$ and $\sigma_K^{\rm expt}$ is still and clearly needed. Yet, neither the nonrelativistic[27] nor the

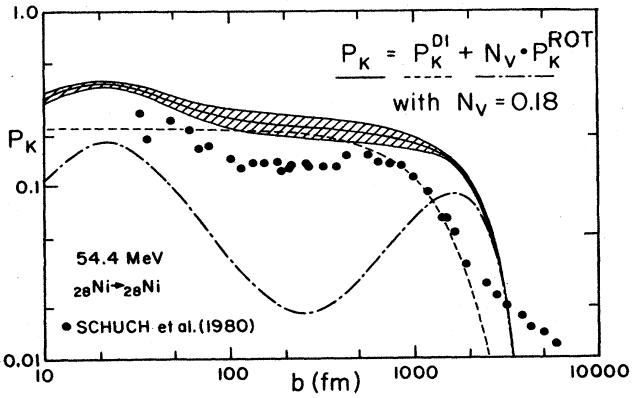

FIG. 3. K-shell vacancy production probability in 54.4-MeV Ni-Ni collision. The dashed curve represents our calculations of the direct-ionization probability; the dash-dotted curve shows the rotational-coupling probability of Ref. 28 multiplied by the $2p\pi$ vacancy fraction N_V. N_V is set here as 0.18 to fit the experimental cross section, $\sigma_K^{\text{expt}}=31$ kb, with $\sigma_K^{\text{DI}}+N_V\sigma_K^{\text{ROT}}$. The data, P_K^{expt}, are from Schuch *et al.* (1980) of Refs. 6 and 26. The solid curve is according to Eq. (14) and using 6.5 keV as the input $\Delta E_{2p}^{\text{obs}}(0)$ in Eq. (13). This curve is surrounded by the band that is bounded by the curves obtained when $\pm 3\%$ change is made in the choice of the $2p\sigma$-state binding energy with the appropriate adjustments of the N_V constant; the lower bound is drawn for $\Delta E_{2p}^{\text{obs}}(0)=6.7$ keV and $N_V=0.2$ and the upper curve in this band obtains when $\Delta E_{2p}^{\text{obs}}(0)=6.3$ keV and $N_V=0.15$.

relativistic[28] evaluation of P_K^{ROT} agrees with the data by itself. We note that the nonrelativistic[27] cross section is $\sigma_K^{\text{ROT}}=158$ kb and the relativistic[28] value is $\sigma_K^{\text{ROT}}=105$ kb.

To account for the experimental results, we propose to add to our nonempirical calculation of direct excitation an empirically scaled rotational-coupling term

$$P_K=P_K^{\text{DI}}+N_V P_K^{\text{ROT}}, \tag{14}$$

where N_V, the empirical vacancy factor[29] is such that $N_V=(\sigma_K^{\text{expt}}-\sigma_K^{\text{DI}})/\sigma_K^{\text{ROT}}$. Consistently with the use of relativistic wave functions in the calculation of σ_K^{DI} we take the relativistic P_K^{ROT} and σ_K^{ROT} of Ref. 28. With $N_V=(31\text{ kb}-12\text{ kb})/105\text{ kb}=0.18$, $N_V P_K^{\text{ROT}}$ is shown in Fig. 3 by the dotted line and P_K of Eq. (14) is represented by the solid curve. Neither direct ionization (dashed curve) nor rotational coupling (dotted curve) alone agrees with the data as well as their sum (solid curve).

IV. DISCUSSION

The addition of probabilities for these two processes is *a posteriori* justified by relatively low probabilities with which these processes deplete the K shell of the united atom. Should either of the probabilities be of order of 1, a correct approach would require a solution to the system of differential equations for the amplitudes, which define the direct-ionization and rotational-coupling excitation probabilities. Attempts have recently been made[30] to solve this system of equations. Our addition of the probabilities in Eq. (14) neglects an interference contribution from the direct-ionization and rotational-coupling excitation amplitudes. This interference could be of importance around 1000 fm in Fig. 3 where the absolute values of these two amplitudes are equal. If it were destructive and significant, the interference term would account for the observed discrepancy between the solid curve and the data in the neighborhood of 1000 fm.

Except for large parameters, the agreement of the solid curve with the data is remarkably good, when one considers the experimental uncertainty of 20%, the error of 30% in the calculation caused by binding-energy uncertainty of 3%, and the 15% uncertainty in the fluorescent yield. The disagreement between experiment and calculation at large impact parameters could reflect the inaccuracy of the screened Coulomb potential,[31] which is worst at large internuclear separations. A more rigorous, *ab initio* calculation would be more accurate. However, the complicating effects of projectile ionizations, outer-shell excitation and promotion would probably make the potentials unreliable at large R. Thus, interpretation of experimental data which depends on large impact-parameter collisions is subject to uncertainty whenever the internuclear potential deviates significantly from the Coulomb potential. It seems that P_K^{expt} (b) ought to be smaller at large b. If so, a smaller value of N_V would have been obtained in our scaling procedure to σ_K^{expt}. Also, a smaller value of N_V would have been extracted at small impact parameters if N_V were allowed to increase at large impact parameters. Schuch *et al.* (1984) in Ref. 6 observe that N_V is significantly enhanced in solid targets due to multiple collisions at large impact parameters. This would lower the solid curve in Fig. 3 toward the data and, hence, result in an even better agreement.

Greenberg *et al.*[22] interpreted total cross sections for single and double K-shell excitation in Ni-Ni collisions from 17.9 to 91.5 MeV in terms of the electron promotion model, but did not take into account direct excitation. It now appears that, at the higher energy range, direct excitation provides a significant fraction of the total excitation cross section. In this range, the agreement between calculation and experiment may have been fortuitous. In the lower half of their energy range, direct excitation would have provided too small a fraction of the excitation, and the MO mechanism is still valid.

In general, the relative contributions of direct and electron promotion to excitation of a given electron shell depend on the details of the collision. Electron promotion is most effective at low collision velocities, high ratio of projectile-to-target atomic number, and when exit channels to empty MO's are open.[4] Direct excitation is most effective at high collision velocities, low projectile charge, small impact parameters, and when exit channels are closed.[4]

In the present case of Ni-Ni collisions at ~ 1 MeV per nucleon, electron promotion predominates. In heavier systems, such as the relativistic systems which produce positrons, direct and multistep excitations are relatively more important processes.[32]

A particular conclusion of the present investigation is the significance of electron promotion in enhancing the shift of the binding energy caused by outer-shell excitation and ionization.

With the phenomenal progress in computer solutions to atomic collision problems our procedure might be ultimately and soon tested by the results of numerical coupled-state calculations. The simplest prototype for symmetric collisions—p-H collisions—has been studied extensively by many theorists after Shakeshaft demonstrated[33] that a coupled-state calculation with a 68-pseudofunction basis set is computationally manageable although it may not give entirely satisfactory results. A search for an optimal basis set is always of supreme importance in these studies. For example, Fritsch and Lin[34] have proposed the modified atomic-orbital (AO+) method which complements the conventional atomic-orbital (AO) sets with united-atom (UA) orbitals. This method might offer valuable insights into the bridge between the SA and UA approaches for slow and symmetric collisions, especially if made variational[35] with respect to electronic translation factors and when scrutinized against the triple-center treatment[36] of p-H collisions. However, it remains to be seen whether these insights pertain when more complex, symmetric collision systems such as Ni-Ni are considered. Efficient numerical schemes which account for many electron effects in symmetric systems, although in development,[37] are still in their infancy.
essentially analytical calculation of the direct K-shell ionization in symmetric collisions. Extensions of this work to more complex L-, M-, and N-shell excitations should shed more light on the relative importance of direct and indirect excitation mechanisms.[38] The validity of our approach becomes better as slower collisions are considered, i.e., as $v_1/v_K \to 0$. We have followed Meyerhof in using the Briggs united-atom model, with a proper evaluation of P_K^{DI} in terms of $P_{1s}^{\mathrm{UA}}(b, \frac{1}{2}v_1)$ and $P_{2p\sigma}^{\mathrm{UA}}(b, \frac{1}{2}v_1)$; we have derived an analytical expression for the ionization of $2p$ electrons in the $m=0$ substate and introduced an iterative method to obtain a relevant value of the binding energy for the united atom, taking into account its excitation, ionization, and correcting for finite internuclear distances. The success of this calculation shows that direct-ionization processes can be understood by combining the atomic and molecular approaches. Even in the $Z_1/Z_2 \sim 1$ and low v_1/v_K regime, first-order Born techniques developed in the separated-atom theories do apply, once properly transfused into the united-atom picture. The first Born approximations, strictly valid in the very asymmetric $Z_1/Z_2 \ll 1$ and fast $v_1/v_K \gg 1$ collisions, are now reconciled with MO theories in the diametrically opposite zone of $Z_1/Z_2 \sim 1$ and $v_1/v_K \ll 1$, where the molecular-orbital schemes apply. To paraphrase the last sentence of Brigg's review article,[39] the usefulness of the united-atom approximation to the MO transition amplitude in the case $Z_1 \sim Z_2$ has by now not only been tested but also well established.

The gap between the regions of validity of MO and first Born approximations in the Madison-Merzbacher diagram (see Fig. 1) at slow collisions disappears once these calculations are modified to account for the perturbed nature of the separated target atom (going from $Z_1/Z_2 \ll 1$ to $Z_1/Z_2 \sim \frac{1}{2}$) or that of the united atom (from $Z_1/Z_2 \sim 1$ to $Z_1/Z_2 \sim \frac{1}{2}$). Thus the field of atomic collisions enters the stage of scientific investigation where islands of understanding coalesce into a more global picture. The white area in Fig. 1 remains *terra incognita*. By coupled-state calculations in a molecular basis, this expanse will perhaps be conquered. For now the asterisk in the forbidden (to the first Born approximation) MO territory in Fig. 1 means a reconciliation between two seemingly opposite treatments of atomic collisions.

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[1]D. H. Madison and E. Merzbacher, in *Atomic Inner-Shell Processes,* edited by B. Crasemann (Academic, New York, 1975), Vol. I, p. 1.

[2]W. Brandt, R. Laubert, and L. Sellin, Phys. Lett. **21**, 518 (1966); Phys. Rev. **151**, 56 (1966); G. Basbas, W. Brandt, and R. H. Ritchie, Phys. Rev. A **7**, 1971 (1973).

[3]The area by which the domain of the SA theory is extended is inferred from successes and failures of the PSS treatment in K-shell data analysis for the systems with an appreciable Z_1/Z_2 ratio.

[4]M. Barat and W. Lichten, Phys. Rev. A **6**, 211 (1972). For a more recent review of the electron promotion model, see W. Lichten, J. Phys. Chem. **84**, 2101 (1980). The dashed boundary of the MO area in Fig. 1 is far more speculative since the MO approach has not as yet been extended in a perturbative treatment.

[5]J. S. Briggs and J. Macek, J. Phys. B **5**, 579 (1972); **6**, 841 (1973); **6**, 982 (1973).

[6]I. Tserruya, H. Schmidt-Böcking, and R. Schuch, Phys. Rev. A **18**, 2482 (1978); S. Hagmann, C. L. Cocke, E. Justiniano, J. R. Macdonald, and H. Schmidt-Böcking, J. Phys. B **12**, L395 (1979); R. Schuch, G. Nolte, and H. Schmidt-Böcking, Phys. Rev. A **22**, 1447 (1980); G. Nolte, J. Volpp, R. Schuch, H. J. Specht, W. Lichtenberg, and H. Schmidt-Böcking, J. Phys. B **13**, 4599 (1980); C. L. Cocke, H. Schmidt-Böcking, and R. Schuch, *ibid.* **15**, 651 (1982); H. Schmidt-Böcking, R. Anholt, R. Schuch, P. Vincent, K. E. Stiebing, and H. U. Jäger, *ibid.* **15**, 3057 (1982); H. Schmidt-Böcking, H. Baumann, K. Bethge, A. Gruppe, W. Schadt, R. Schuch, and K. E. Steibing, Z. Phys. A **304**, 177 (1982); D. Maor, D. Liesen, P. H. Mokler, B. Rosner, H. Schmidt-Böcking, and R. Schuch, Phys. Rev. A **27**, 2881 (1983); R. Schuch, E. Jaustiniano, R.

Hoffmann, W. Schadt, H. Schmidt-Böcking, P. H. Mokler, F. Bosch, W. A. Schonfeldt, and Z. Stachura, J. Phys. B **16**, 2029 (1983); R. Schuch, R. Hoffmann, K. Müller, E. Pflanz, H. Schmidt-Böcking, and H. J. Specht, Z. Phys. A **316**, 5 (1984); K. E. Steibing, H. Schmidt-Böcking, W. Schadt, K. Bethge, R. Schuch, P. H. Mokler, F. Bosch, D. Liesen, S. Hagmann, and P. Vincent, *ibid.* **319**, 239 (1984).

[7]W. E. Meyerhof, in *Electronic and Ionic Collisions,* edited by N. Oda and K. Takayanagi (North-Holland, Amsterdam, 1979), p. 676.

[8]C. H. Annett, B. Curnutte, and C. L. Cocke, Phys. Rev. A **19**, 1038 (1979); N. Luz, S. Sackmann, and H. O. Lutz, J. Phys. B **12**, 1973 (1979); R. Anholt, C. Stroller, and W. E. Meyerhof, *ibid.* **13**, 3807 (1980); A. Chetioui, J. P. Rozet, J. P. Briant, and C. Stephen, *ibid.* **14**, 1625 (1981); J. Stahler and G. Presser, *ibid.* **14**, 4093 (1981); D. Maor, *ibid.* **15**, L395 (1982).

[9]W. E. Meyerhof, Phys. Rev. A **18**, 414 (1978); **20**, 2235 (1979).

[10]J. S. Briggs, J. Phys. B **8**, L485 (1975).

[11]V. Zoran, A. Berinde, and D. Fluerasu, in *Proceedings of the International Seminar on High-Energy Ion-Atom Collision Processes, Debrecen, Hungary, 1981,* edited by D. Berényi and G. Hock (Elsevier, Amsterdam, 1982), p. 221; also J. Phys. B **15**, 2047 (1982).

[12]P. A. Amundsen, J. Phys. B **11**, L737 (1978); D. H. Jakubassa-Amundsen, Phys. Scr. **26**, 319 (1982); Z. Phys. A **315**, 21 (1984).

[13]J. M. Hansteen, O. M. Johansen, and L. Kocbach, At. Data Nucl. Data Tables **15**, 305 (1975).

[14]W. Brandt and G. Lapicki, Phys. Rev. A **10**, 474 (1974). Equation (12) in this reference is in error and should be replaced by Eq. (5) of the present paper; see also Eq. (A10) in G. Lapicki and W. Losonsky, Phys. Rev. A **15**, 896 (1977).

[15]See Eqs. (7) and (9) of Ref. 14.

[16]L. Kocbach, J. M. Hansteen, and R. Gundersen, Phys. Scr. **27**, 54 (1983). These tables supersede Ref. 13 since they allow for a more accurate interpolation of $P_{2p}(b)$ and report $P_{2p\sigma}$ and $P_{2p\pi}$ separately. These tables apply only to $v_1/v_K > 0.25$ collisions.

[17]B.-H. Choi and E. Merzbacher, Phys. Rev. **177**, 233 (1969).

[18]L. Kocbach, J. Phys. B **9**, 2269 (1976).

[19]T. A. Carlson, C. C. Lu, T. C. Tucker, C. W. Nestor, Jr., and F. B. Malik, Oak Ridge National Laboratory Report No. 4614 (1971, unpublished) (available from National Technical Information Service, Springfield, VA 22151 for $3.00); see also C. C. Lu, T. A. Carlson, F. B. Malik, T. C. Tucker, and C. W. Nestor, Jr., At. Data **3**, 1 (1971).

[20]T. A. Carlson, C. W. Nestor, Jr., N. Wasserman, and J. D. McDowell, At. Data, **2**, 63 (1970).

[21]H.-D. Betz, Rev. Mod. Phys. **44**, 465 (1972).

[22]J. S. Greenberg, P. Vincent, and W. Lichten, Phys. Rev. A **16**, 964 (1977).

[23]B. Müller and W. Greiner, Z. Naturforsch. **319**, 1 (1976). Calculations of $\Delta E_S(R)$ can be tested in predictions of the phase difference between the $2p\sigma$ and $1s$ states; interference effects, observed with the hydrogenic projectiles in K-to-K shell vacancy transfer probability [R. Schuch, H. Ingwersen, E. Justiniano, H. Schmidt-Böcking, M. Schulz, and F. Ziegler, J. Phys. B **17**, 2319 (1984); B. Ficke, W.-D. Sepp, and T. Morović, Z. Phys. A **318**, 369 (1984)], allow for an experimental verification of these calculations.

[24]G. Lapicki and A. R. Zander, Phys. Rev. A **23**, 2072 (1981).

[25]W. Brandt and G. Lapicki, Phys. Rev. A **23**, 1717 (1981).

[26]The data shown in Fig. 2 of the Schuch *et al.* (1980) paper (see Ref. 6) were made available to us in tabular form by H. Schmidt-Böcking.

[27]K. Taulbjerg, J. S. Briggs, and J. Vaaben, J. Phys. B **9**, 1351 (1976).

[28]D. H. Jakubassa and K. Taulbjerg, J. Phys. B **13**, 757 (1980), and D. H. Jakubassa-Amundsen (private communication).

[29]As suggested recently by M. Meron, D. Maor, and B. Rosner, J. Phys. B **16**, 3983 (1983); M. Meron and B. Rosner, Phys. Rev. A **30**, 132 (1984), a study of charge-state distributions due to inner- and outer-shell collisions may yield an independent estimate of N_V.

[30]D. H. Jakubassa-Amundsen, P. A. Amundsen, and K. Aashamar, J. Phys. B **16**, 1047 (1983).

[31]N. Bohr, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd. **18**, 8 (1948).

[32]G. Soff, W. Greiner, W. Betz, and B. Müller, Phys. Rev. A **20**, 169 (1979); D. Maor, Z. Stachura, P. H. Mokler, B. Liu, and D. Liesen, J. Phys. B **16**, L733 (1983); T. H. J. de Reus, J. Reinhardt, B. Müller, W. Greiner, G. Soff, and U. Müller, *ibid.* **17**, 615 (1984).

[33]R. Shakeshaft, Phys. Rev. A **18**, 1930 (1978).

[34]W. Fritsch and C. D. Lin, Phys. Rev. A **29**, 3039 (1984) and references therein.

[35]D. S. F. Crothers and J. G. Hughes, Comments At. Mol. Phys. **15**, 15 (1984) and references therein.

[36]T. G. Winter and C. D. Lin, Phys. Rev. A **29**, 3071 (1984); **30**, 3323 (E) (1984).

[37]N. Grün, A. Mülhaus, and W. Scheid, J. Phys. B **15**, 4043 (1983); H. J. Lüdde and R. M. Dreizler, *ibid.* **16**, 3973 (1983); J. F. Reading, A. L. Ford, J. S. Smith, J. Alexander, and R. L. Becker, Nucl. Instrum. Methods B **4**, 266 (1984); H. J. Lüdde and R. M. Dreizler, J. Phys. B **18**, 107 (1985).

[38]R. Shanker, R. Bilau, R. Hippler, U. Wille, and H. O. Lutz, J. Phys. B **14**, 997 (1981); P. H. Woerlee, R. J. Fortner, and F. W. Saris, *ibid.* **14**, 3175 (1981); D. Schneider, G. Nolte, U. Wille, and N. Stolterfoht, Phys. Rev. A **28**, 161 (1983); C. Courbin-Gaussorgues, V. Sidis, and J. Vaaben, J. Phys. B **16**, 2817 (1983); R. Schanker, R. Hippler, U. Wille, R. Bilau, and H. O. Lutz, Z. Phys. **313**, 281 (1983); R. Shanker, R. Hippler, R. Bilau, and H. O. Lutz, Phys. Lett. **99A**, 313 (1983); Z. Stachura, F. Bosch, F. J. Hambsch, B. Liu, D. Maor, P. H. Mokler, W. A. Schönfeldt, W. Wahl, B. Cleff, M. Brussermann, and J. Wigger, J. Phys. B **17**, 835 (1984); A. A. Antar and Q. C. Kessel, Phys. Rev. A **29**, 1070 (1984); U. Wille and R. Hippler, Comments At. Mol. Phys. **14**, 255 (1984); R. Shanker, U. Wille, R. Bilau, R. Hippler, W. R. McMurray, and H. O. Lutz, J. Phys. B **17**, 1353 (1984); P. H. Mokler, D. H. H. Hoffmann, W. A. Schönfeldt, D. Maor, W. E. Meyerhof, and Z. Stachura, *ibid.* **17**, 4499; Nucl. Instrum. Methods B **4**, 34 (1984); T. Tonuma, M. Kase, T. Kambara, H. Kumagai, T. Matsuo, J. Urakawa, H. Shibata, J. Takahashi, S. Özök, S. H. Be, I. Kohino, and H. Tawara, J. Phys. B **17**, L317 (1984).

[39]J. S. Briggs, Rep. Prog. Phys. **39**, 217 (1976).