

Distorted atomic orbital expansion for slow ion-atom collisions

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Distorted atomic orbital method, proposed by Kobayashi, Ishihara and Toshima [*Muon Catalyzed Fusion* **2**, 191 (1988)], is applied to low energy ion-atom collisions. This method is free from the difficulty of spurious couplings. The basic idea of the method is discussed in detail. An iterative method for the numerical calculation is developed and, as an example, quantum mechanical calculation of $\text{He}^{2+} + \text{H}$ collisions for incident energy $E_i \leq 200$ eV is carried out. Calculated cross section connects naturally to those obtained from a corresponding semiclassical calculation for $E_i \geq 200$ eV [T. G. Winter and G. J. Hatton, *Phys. Rev. A* **21**, 793 (1980)].

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I. INTRODUCTION

The molecular orbital expansion has been a standard theoretical method for slow ion-atom collisions [1]. It is well known that the total wave function in this expansion does not satisfy the asymptotic boundary conditions because of the use of the internuclear coordinates to describe the relative motion of projectile and target. As a result, the coupled equations for the relative motion may contain spurious long-range coupling terms. This difficulty can be avoided in the semiclassical approximation by introducing the so-called electron translation factors in the molecular orbitals. However, for very low energies where a full quantum mechanical treatment is required there is, to our knowledge, no practical method available for ion-atom collisions.

The difficulty of spurious couplings does not occur if the correct relative coordinates between projectile and target are used instead of internuclear coordinates to describe the relative motion in the asymptotic region. Such an approach has been proposed by Kobayashi, Ishihara and Toshima [2] and applied successfully to the collision processes involving muonic atoms. The above authors expand the wave function in terms of adiabatic basis functions defined by fixing the relative coordinates of each arrangement channel. In this paper we further develop this method for its application to low energy ion-atom collisions.

Since only a brief description of the method is given in Ref. [2], we give a detailed discussion of the basic idea as well as the fundamental analytical formulas in Section II. In Section III, we develop a method to solve the coupled integro-differential equations obtained for the relative motion. As a numerical example, the method is applied to $\text{He}^{2+} + \text{H}$ collisions in Section IV.

II. FORMULATION

A. Preliminary considerations

Consider the three body process

$$B + (A, e) \rightarrow B + (A, e) \quad (1)$$

$$\rightarrow A + (B, e) \quad (2)$$

where e is the electron, A and B are bare nuclei with masses M_A and M_B , and charges Z_A and Z_B . We use atomic units unless otherwise stated. The total Hamiltonian in the center of mass coordinate system is written in terms of Jacobi coordinates $(\mathbf{R}_A, \mathbf{r}_A)$ and $(\mathbf{R}_B, \mathbf{r}_B)$ shown in Fig. 1 for arrangement channel (1) and (2)

$$\begin{aligned} H &= -\frac{1}{2\mu_A} \nabla_{\mathbf{R}_A}^2 - \frac{1}{2m_A} \nabla_{\mathbf{r}_A}^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R}, \\ &= -\frac{1}{2\mu_B} \nabla_{\mathbf{R}_B}^2 - \frac{1}{2m_B} \nabla_{\mathbf{r}_B}^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R}, \end{aligned} \quad (3)$$

where reduced masses are defined by

$$\begin{aligned} \mu_A &= \frac{(1 + M_A)M_B}{1 + M_A + M_B}, & m_A &= \frac{M_A}{1 + M_A}, \\ \mu_B &= \frac{(1 + M_B)M_A}{1 + M_A + M_B}, & m_B &= \frac{M_B}{1 + M_B}, \end{aligned} \quad (4)$$

and R is the internuclear distance.

We define adiabatic basis functions for each channel, considering \mathbf{R}_α ($\alpha = A, B$) as a fixed parameter, by

$$[h_\alpha - E_{\beta n \nu}^\alpha(R_\alpha)] \psi_{\beta n \nu}^\alpha(\mathbf{r}_\alpha; \mathbf{R}_\alpha) = 0, \quad (5)$$

$$h_\alpha = -\frac{1}{2m_\alpha} \nabla_{\mathbf{r}_\alpha}^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R}. \quad (6)$$

As $R_\alpha \rightarrow \infty$, the eigenstates $\psi_{\beta n \nu}^\alpha$ becomes a state localized around the center A or B. $\beta = A$ or B discriminates these two, n is the principal quantum number and ν

the other quantum numbers of this atomic state. We do not consider the completely symmetric case, i.e., when $Z_A = Z_B$ and $M_A = M_B$.

The energy eigenvalue $E_{\beta n\nu}^\alpha(R_\alpha)$ of Eq. (5) in the separated atom limit $R_\alpha \rightarrow \infty$, is given by

$$\begin{aligned} E_{\beta n\nu}^\alpha(\infty) &= -\frac{Z_\alpha^2 m_\alpha}{2n^2} \quad (\beta = \alpha) \\ &= -\frac{Z_\beta^2/m_\alpha}{2n^2} \quad (\beta \neq \alpha). \end{aligned} \quad (7)$$

The second line of Eq. (7) is obtained by using the transformation $\nabla_{\mathbf{r}_\alpha} = m_\alpha \nabla_{\mathbf{r}_\beta}$ derived from the relation $\mathbf{r}_\beta = m_\alpha \mathbf{r}_\alpha \mp \mathbf{R}_\alpha$ where the upper and lower sign are for $\alpha = A$ and $\alpha = B$, respectively. For $\beta = \alpha$, the eigenvalue and the eigenfunction

$$\begin{aligned} E_{\alpha n\nu}(R_\alpha) &\equiv E_{\alpha n\nu}^\alpha(R_\alpha), \\ \psi_{\alpha n\nu}(\mathbf{r}_\alpha; \mathbf{R}_\alpha) &\equiv \psi_{\alpha n\nu}^\alpha(\mathbf{r}_\alpha; \mathbf{R}_\alpha) \end{aligned} \quad (8)$$

become in the limit of $R_\alpha \rightarrow \infty$ those of an isolated atom where the finite nuclear mass effect is taken into account. $\psi_{\alpha n\nu}$ is the atomic orbital with the static distortion by the nucleus $\beta (\neq \alpha)$ fully taken into account. On the other hand, $\psi_{\beta n\nu}^\alpha$ with $\beta \neq \alpha$ has no physical meaning because it does not describe a correct (β, e) atom at the limit $R_\alpha \rightarrow \infty$ and the distortion at a finite R_α is not for fixed relative distance R_β .

In the expansion of the total three body wave function Ψ in terms of $\{\psi_{A n\nu}\}$ and $\{\psi_{B n\nu}\}$

$$\Psi = \sum_{n\nu} F_{A n\nu}(\mathbf{R}_A) \psi_{A n\nu}(\mathbf{r}_A; \mathbf{R}_A) + \sum_{n\nu} F_{B n\nu}(\mathbf{R}_B) \psi_{B n\nu}(\mathbf{r}_B; \mathbf{R}_B), \quad (9)$$

the relative motion of projectile and target is described by Jacobi coordinates in each arrangement channel and, therefore, the coupled equations for $F_{A n\nu}$ and $F_{B n\nu}$ do not contain spurious coupling terms. All three Coulomb interactions are included in the channel Hamiltonians h_A and h_B that define the basis functions as it is the case in

the usual molecular orbital (MO) expansion. Expansion (9) may thus be considered to be the MO expansion without difficulty of spurious couplings.

However, the above expansion contains a serious difficulty due to the lack of completeness of the basis sets $\{\psi_{An\nu}, \psi_{Bn'\nu'}\}$. In the MO-limit, i.e., the infinite nuclear mass limit $M_A, M_B \rightarrow \infty$, $\mathbf{R}_A = \mathbf{R}_B$ and $h_A = h_B$ hold and, therefore, the eigenfunctions $\psi_{\beta n\nu}^A$ and $\psi_{\beta n\nu}^B$ of Eq. (5) become identical. Since M_A and M_B are much larger than the electron mass, $\psi_{\beta n\nu}^A$ and $\psi_{\beta n\nu}^B$ are both very close to the MO-limit. Thus we can examine the completeness of our basis sets $\{\psi_{An\nu}, \psi_{Bn'\nu'}\}$ by comparing them with the MO-limit, because the non-crossing rule holds in this limiting procedure.

Consider the states that have the same asymptotic energy as $E_{An\nu}^A(\infty)$ in the MO-limit where $m_\alpha = 1$ in Eq. (7). They are $n(n+1)/2$ fold degenerate $E_{An\nu}^A(\infty)$ and $E_{An\nu}^B(\infty)$, and $n'(n'+1)/2$ fold degenerate $E_{Bn'\nu'}^A(\infty)$ and $E_{Bn'\nu'}^B(\infty)$ with $n' = nZ_B/Z_A$. Thus the number of degenerate states in the MO-limit are $n(n+1) + n'(n'+1)$. We did not count the degeneracy with respect to the sign of the angular momentum component along \mathbf{R}_α . Since $m_\alpha < 1$ in Eq. (7), the states we include in our basis sets $\{\psi_{An\nu}, \psi_{Bn'\nu'}\}$ always have higher energies than those we do not,

$$\begin{aligned} E_{An\nu}(\infty) &> E_{Bn'\nu'}^A(\infty), \\ E_{Bn'\nu'}(\infty) &> E_{An\nu}^B(\infty). \end{aligned} \quad (10)$$

Energy spectra of h_A and h_B are shown schematically in Fig. 2 for a symmetric charge system ($Z_A = Z_B$) and an asymmetric system ($Z_A = 1$ and $Z_B = 2$). Solid lines are those included in the basis sets $\{\psi_{An\nu}, \psi_{Bn'\nu'}\}$ and dashed lines are those not included. Adiabatic potentials $E_{\beta n\nu}^A(R_A)$ and $E_{\beta n'\nu'}^B(R_B)$ for h_A and h_B , respectively, both correspond one-to-one to the potential curves in the MO-limit counting from the bottom. We see that for $Z_A = Z_B$ the states corresponding to the same states in the MO-limits are either taken twice or missing in the basis sets. For the case of $Z_A = 1$

and $Z_B = 2$, the state corresponding to the second level of MO-limit is missing and the fifth level is taken twice, and so on.

The basis sets $\{\psi_{An\nu}, \psi_{Bn'\nu'}\}$ of the expansion (9) are far from complete because they are not complete in the MO-limit. This is the difficulty in the expansion (9).

B. Distorted orbital expansion

We have seen above that the incompleteness of the basis sets of expansion (9) is closely related to the inequality (10) which is inevitable if we take full account of distortion of the atomic orbital due to the existence of the other ion. Asymptotic energy $E_{\beta n\nu}^\alpha(\infty)$ ($\beta \neq \alpha$) of the unphysical state is determined by Z_β , while that of physical state, $E_{\alpha n\nu}(\infty)$, does not depend on Z_β . Therefore we can make the basis sets complete in the MO-limit by varying Z_β without affecting the asymptotic energy of the physical state $\psi_{\alpha n\nu}$.

We define $\psi_{An\nu}$ and $\psi_{Bn\nu}$ as eigenfunctions of

$$\begin{aligned} h_A &= -\frac{1}{2m_A}\nabla_{r_A}^2 - \frac{Z_A}{r_A} - \frac{m_A Q_B}{r_B} \\ h_B &= -\frac{1}{2m_B}\nabla_{r_B}^2 - \frac{m_B Q_A}{r_A} - \frac{Z_B}{r_B} \end{aligned} \quad (11)$$

with physical dissociation limits. We call them distorted atomic orbitals (DAO's). Q_A and Q_B are adjustable parameters to be chosen to make the basis sets $\{\psi_{An\nu}, \psi_{Bn'\nu'}\}$ complete in the MO-limit and yet to take account of as much distortion as possible. We have not included the internuclear interaction in the DAO Hamiltonian (11), because its effect in the wave function is smaller than that of the adjustment of a nuclear charge.

The DAO Hamiltonian (11) can be written in the form

$$h_A = m_A \left(-\frac{1}{2}\nabla_{x_A}^2 - \frac{Z_A}{|\mathbf{x}_A|} - \frac{Q_B}{|\mathbf{x}_A - \mathbf{R}_A|} \right)$$

$$h_B = m_B \left(-\frac{1}{2} \nabla_{\mathbf{x}_B}^2 - \frac{Q_A}{|\mathbf{x}_B + \mathbf{R}_B|} - \frac{Z_B}{|\mathbf{x}_B|} \right) \quad (12)$$

using $\mathbf{x}_\alpha = m_\alpha \mathbf{r}_\alpha$ instead of \mathbf{r}_α . They are similar to the MO Hamiltonian and exact eigenfunctions

$$\psi_{\alpha n \nu}(\mathbf{r}_\alpha; \mathbf{R}_\alpha) = \psi_{\alpha n q m}(\xi_\alpha, \eta_\alpha; R_\alpha) \frac{1}{\sqrt{2\pi}} e^{im\phi_\alpha} \quad (13)$$

are obtained by separation of variables using the spheroidal coordinates

$$\begin{aligned} \xi_A &= \frac{x_A + r_B}{R_A}, & \eta_A &= \frac{x_A - r_B}{R_A}, \\ \xi_B &= \frac{r_A + x_B}{R_B}, & \eta_B &= \frac{r_A - x_B}{R_B}, \end{aligned} \quad (14)$$

and the azimuthal angle ϕ_α of \mathbf{r}_α around \mathbf{R}_α . The quantum numbers q and m are those of the separated atom limit, namely, a parabolic quantum number (number of nodes along the variable ξ_α) $q = 0, 1, \dots, n - m - 1$, and the magnetic quantum number $m = 0, 1, \dots, n - 1$.

As for the choice of parameters Q_A and Q_B , we see from Eq. (12) a condition

$$\frac{Q_B}{Z_A} = \frac{Z_B}{Q_A}, \quad (15)$$

for example, makes DAO's complete in the MO-limit since the correlation diagrams for h_A and h_B become similar. Adopting this condition, we still have one more freedom to determine Q_A and Q_B . A specific example is given in section IV.

We now make an expansion of the total wave function in terms of DAO's given by Eq. (13). The total angular momentum (J, M) and the total parity p are good quantum numbers of the total Hamiltonian H given by Eq. (3). The total wave function $\Psi^{JM p}$ for a given set of quantum numbers (J, M, p) is expanded in the form

$$\Psi^{JM p} = \sum_{n\nu} \frac{\chi_{A n \nu}(R_A)}{R_A} \psi_{A n \nu}^{JM p}(\tau_A; R_A) + \sum_{n\nu} \frac{\chi_{B n \nu}(R_B)}{R_B} \psi_{B n \nu}^{JM p}(\tau_B; R_B), \quad (16)$$

where $\tau_\alpha = (\hat{R}_\alpha, \mathbf{r}_\alpha)$ and

$$\psi_{\alpha n \nu}^{JM p}(\tau_\alpha; R_\alpha) = \psi_{\alpha n q m}(\xi_\alpha, \eta_\alpha; R_\alpha) \mathcal{D}_m^{JM p}(\phi_\alpha, \Theta_\alpha, \Phi_\alpha), \quad (17)$$

with

$$\begin{aligned} \mathcal{D}_m^{JM p}(\phi_\alpha, \Theta_\alpha, \Phi_\alpha) = & \frac{1}{4\pi} \sqrt{\frac{2J+1}{1+\delta_{0m}}} [D_{-m, -M}^J(\phi_\alpha, \Theta_\alpha, \Phi_\alpha) \\ & + p(-)^{J+m} D_{m, -M}^J(\phi_\alpha, \Theta_\alpha, \Phi_\alpha)]. \end{aligned} \quad (18)$$

D_{mM}^J is the Wigner's D-function [3], and Θ_α and Φ_α are the polar and the azimuthal angle of \mathbf{R}_α . In the expansion (16), we have chosen $\phi_\alpha = 0$ to be the direction of X-axis after two successive Eulerian rotations of the space fixed coordinates, i.e., a rotation Φ_α about Z-axis followed by a rotation Θ_α about the rotated X-axis. Substituting Eq. (16) into the Schrödinger equation

$$(H - E)\Psi^{JM p} = 0, \quad (19)$$

we obtain a set of coupled integro-differential equations for the radial wave functions $\chi_{\alpha n \nu}(R_\alpha)$,

$$\begin{aligned} -\frac{d^2 \chi_{\alpha n \nu}(R_\alpha)}{dR_\alpha^2} + \sum_{n'\nu'} [U_{\alpha n \nu, \alpha n' \nu'}^{(0)}(R_\alpha) + 2P_{\alpha n \nu, \alpha n' \nu'}^{(0)}(R_\alpha) \frac{d}{dR_\alpha}] \chi_{\alpha n' \nu'}(R_\alpha) \\ + \sum_{n'\nu'} \int d\tau_\alpha [\psi_{\alpha n \nu}^{JM p}(\tau_\alpha; R_\alpha)]^* [2\mu_\beta R_\beta (H - E) \frac{\chi_{\beta n' \nu'}(R_\beta)}{R_\beta} \psi_{\beta n' \nu'}^{JM p}(\tau_\beta; R_\beta)] = 0, \end{aligned} \quad (20)$$

where E is the total energy in the center of mass system, matrix elements $U_{\alpha n \nu, \alpha n' \nu'}^{(0)}(R_\alpha)$ and $P_{\alpha n \nu, \alpha n' \nu'}^{(0)}(R_\alpha)$ are defined by Eq. (27). $\psi_{\alpha n \nu}^{JM p}(\tau_\alpha; R_\alpha)$ is assumed to be normalized as

$$\int |\psi_{\alpha n \nu}^{JM p}(\tau_\alpha; R_\alpha)|^2 d\tau_\alpha = 1 \quad (21)$$

with the volume element $d\tau_\alpha = d\hat{R}_\alpha d\mathbf{r}_\alpha$.

III. METHOD OF SOLUTION

Direct numerical solution of Eq. (20) is difficult because of the unknown functions $\chi_{\beta n' \nu'}[R_\beta(\tau_\alpha, R_\alpha)]$ that appear in the term to be integrated over τ_α . We describe in this section the method we have developed to solve Eq. (20) by transforming it into a set of differential equations.

Let us expand the unknown function $\chi_{\beta n' \nu'}(R_\beta)$ around R_α which is not an integration variable in the third term of Eq. (20),

$$\chi_{\beta n' \nu'}(R_\beta) = \sum_{t=0}^{\infty} \frac{[\Delta_{\beta\alpha}(\tau_\alpha, R_\alpha)]^t}{t!} \frac{d^t}{dR_\alpha^t} \chi_{\beta n' \nu'}(R_\alpha), \quad (22)$$

where

$$\Delta_{\beta\alpha}(\tau_\alpha, R_\alpha) = R_\beta(\tau_\alpha, R_\alpha) - R_\alpha \quad (23)$$

is the difference between the lengths of the Jacobi vectors \mathbf{R}_α and \mathbf{R}_β . Expansion (22) may be interpreted physically to be that in the power of the ratio, v/v_e , of the relative velocity to the electron orbital velocity. Since we are interested in slow collisions, i.e., when $v/v_e \ll 1$, we truncate the expansion (22) at the term with $t = T$.

The integrand in the third term of Eq. (20) can be expressed in terms of $\chi_{\beta n' \nu'}(R_\beta)$ and its first and second derivatives with respect to R_β in the following form,

$$\begin{aligned} & 2\mu_\beta R_\beta (H - E) \frac{\chi_{\beta n' \nu'}(R_\beta)}{R_\beta} \psi_{\beta n' \nu'}^{JM_p}(\tau_\beta; R_\beta) \\ &= \left[\frac{d^2 \chi_{\beta n' \nu'}(R_\beta)}{d^2 R_\beta} + 2 \frac{d \chi_{\beta n' \nu'}(R_\beta)}{d R_\beta} \hat{P}_\beta + \chi_{\beta n' \nu'}(R_\beta) \hat{U}_\beta \right] \psi_{\beta n' \nu'}^{JM_p}(\tau_\beta; R_\beta). \end{aligned} \quad (24)$$

The explicit forms of the operator \hat{U}_β and \hat{P}_β entering the right hand side of Eq. (24) are given in the Appendix. They do not contain the derivative operator $\partial/\partial R_\beta$. Using Eq. (24) and the truncated expansion (22), the coupled integro-differential equations become a set of differential equations of $(T + 2)$ th order. Since these equations no longer contain non-local couplings, we can use a common independent variable r

for both channels. The coupled differential equations so obtained can be written in matrix notation as

$$[-S^{(0)}(r)\frac{d^2}{dr^2} + 2P^{(0)}(r)\frac{d}{dr} + U^{(0)}(r)]\chi(r) + \lambda\mathbf{V}_T(r) = 0 \quad (25)$$

where

$$\mathbf{V}_T(r) = \sum_{t=1}^T [-S^{(t)}(r)\frac{d^2}{dr^2} + 2P^{(t)}(r)\frac{d}{dr} + U^{(t)}(r)]\frac{d^t}{dr^t}\chi(r). \quad (26)$$

We have introduced in Eq. (25) a scaling parameter λ , with $\lambda = 1$ describing the physical situation of our interest. Elements of the $S^{(t)}(r)$, $P^{(t)}(r)$ and $U^{(t)}(r)$ matrices ($t = 0, 1, 2, \dots$) are defined by the following expressions.

$$\begin{aligned} S_{\alpha\nu, \alpha'n'\nu'}^{(t)}(R_\alpha) &= \int d\tau_\alpha \omega_{\alpha\alpha'}^{(t)} [\psi_{\alpha\nu}^{JM_p}(\tau_\alpha; R_\alpha)]^* \psi_{\alpha'n'\nu'}^{JM_p}(\tau_{\alpha'}; R_{\alpha'}), \\ P_{\alpha\nu, \alpha'n'\nu'}^{(t)}(R_\alpha) &= \int d\tau_\alpha \omega_{\alpha\alpha'}^{(t)} [\psi_{\alpha\nu}^{JM_p}(\tau_\alpha; R_\alpha)]^* \hat{P}_{\alpha'} \psi_{\alpha'n'\nu'}^{JM_p}(\tau_{\alpha'}; R_{\alpha'}), \\ U_{\alpha\nu, \alpha'n'\nu'}^{(t)}(R_\alpha) &= \int d\tau_\alpha \omega_{\alpha\alpha'}^{(t)} [\psi_{\alpha\nu}^{JM_p}(\tau_\alpha; R_\alpha)]^* \hat{U}_{\alpha'} \psi_{\alpha'n'\nu'}^{JM_p}(\tau_{\alpha'}; R_{\alpha'}), \end{aligned} \quad (27)$$

where

$$\begin{aligned} \omega_{\alpha\alpha'}^{(t)} &= \frac{\mu_\alpha R_\alpha}{\mu_{\alpha'} R_{\alpha'}} \frac{(\Delta_{\alpha'\alpha})^t}{t!} \quad (t \neq 0), \\ &= \frac{\mu_\alpha R_\alpha}{\mu_{\alpha'} R_{\alpha'}} \quad (t = 0). \end{aligned} \quad (28)$$

Equation (25) is a $(T + 2)$ th order differential equation for the vector function $\chi(r)$. We have designed iterative method for its solution based on the assumption that \mathbf{V}_T is small. As a first step, we neglect $\lambda\mathbf{V}_T(r)$ in Eq. (25) and by taking 1st, 2nd, \dots , T th derivatives of the resulting equation we obtain a set of T algebraic equations that relate the derivatives $d^t\chi/dr^t$ of $\chi(r)$ with $t = 0, 1, \dots, (T + 2)$. We use them to express higher derivatives with $t = 3, 4, \dots, (T + 2)$ in terms of lower derivatives with $t = 0, 1, 2$. Substituting these expressions into Eq. (26) we obtain $\mathbf{V}_T(r)$ that is correct to order λ^0 in the following form.

$$\mathbf{V}_T(r) = [-\bar{S}^{(1)}(r)\frac{d^2}{dr^2} + 2\bar{P}^{(1)}(r)\frac{d}{dr} + \bar{U}^{(1)}(r)]\chi(r) + O(\lambda) \quad (29)$$

We now plug this $\mathbf{V}_T(r)$ back into Eq. (25) and take derivatives of the resulting second order differential equation. We repeat the above procedure to obtain the expression for $\mathbf{V}_T(r)$ to order λ . After L iterations, we obtain $\mathbf{V}_T(r)$ in the form

$$\mathbf{V}_T(r) = [-\bar{S}^{(L)}(r)\frac{d^2}{dr^2} + 2\bar{P}^{(L)}(r)\frac{d}{dr} + \bar{U}^{(L)}(r)]\chi(r) + O(\lambda^L) \quad (30)$$

where the matrices $\bar{S}^{(L)}(r)$, $\bar{P}^{(L)}(r)$ and $\bar{U}^{(L)}(r)$ are given in terms of derivatives of the known matrices $S^{(t)}(r)$, $P^{(t)}(r)$ and $U^{(t)}(r)$ with $t = 0, \dots, T$ defined by Eq. (27). Substituting Eq. (30) into Eq. (25) we obtain the following second order differential equation for $\chi(r)$.

$$\left[-\frac{d^2}{dr^2} + 2P(r)\frac{d}{dr} + U(r)\right]\chi(r) + O(\lambda^{L+1}) = 0, \quad (31)$$

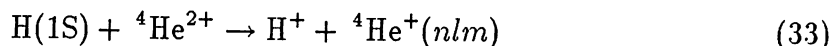
where

$$\begin{aligned} P(r) &= S(r)^{-1}[P^{(0)}(r) + \lambda\bar{P}^{(L)}(r)], \\ U(r) &= S(r)^{-1}[U^{(0)}(r) + \lambda\bar{U}^{(L)}(r)], \\ S(r) &= S^{(0)}(r) + \lambda\bar{S}^{(L)}(r). \end{aligned} \quad (32)$$

We have described a method to obtain the coupled second order differential equations (31) for the radial wave function $\chi_{\alpha\nu}(r)$ by differentiating the coupling terms appearing in the coupled integro-differential equations (20). These differential equations are made more and more accurate simply by consecutive differentiations of coupling terms. The differential equations (31) are to be solved numerically after convergence of the coupling terms, Eq. (32), is reached.

IV. NUMERICAL EXAMPLE

As a numerical example of our method, we have calculated cross sections for the charge transfer process



for the incident energy $E_i = 20\text{--}200$ eV in the center of mass system. Since we are dealing with the extremely low energy region, we use 4-state expansion in the distorted atomic orbital (DAO) given in table I. The united atom designation of the corresponding MO-limit is shown in the third column. We regard H^+ as the nucleus A and ${}^4\text{He}^{2+}$ as B .

As for the choice of parameters Q_A and Q_B defined in Eq. (11), we adopt the condition (15) to ensure the completeness of the DAO basis set in the MO-limit. In addition we impose the condition

$$m_B(Z_A - m_B Q_A) + (1 - m_B)Z_A Z_B = 0 \quad (34)$$

to completely specify these parameters. The Coulomb interaction omitted in the DAO Hamiltonian h_B is

$$\Delta V_B = -\frac{Z_A}{r_A} + \frac{m_B Q_A}{r_A} + \frac{Z_A Z_B}{R}. \quad (35)$$

The condition (34) is to eliminate the leading (dipole) term of Eq. (35) in the asymptotic region $R_B \rightarrow \infty$. We cannot eliminate the dipole couplings in the both arrangement channels. We have chosen the final channel because for the process (33) more states couple in it than in the initial channel.

The boundary conditions for the radial wave function $\chi_{\alpha n q m}(R_\alpha)$ for $R_\alpha \rightarrow \infty$ is

$$\begin{aligned} \chi_{\alpha n q m}(R_\alpha) \rightarrow & \delta_{\alpha A} \frac{1}{k_{A1}} \sin(k_{A1} R_A - \frac{J\pi}{2}) \\ & + f_{\alpha n q m}^{(J)} \exp[i(k_{\alpha n} R_\alpha - \zeta_{\alpha n} \ln 2k_{\alpha n} R_\alpha - \frac{J\pi}{2})] \end{aligned} \quad (36)$$

for parity $p = (-)^J$. States with $p = (-)^{J+1}$ do not occur in the process (33). In Eq. (36),

$$k_{\alpha n} = \sqrt{2\mu_\alpha(E - E_{\alpha n}(\infty))} \quad (37)$$

is the relative momentum,

$$\zeta_{\alpha n} = \frac{\mu_{\alpha}(Z_{\alpha} - 1)}{k_{\alpha n}} \quad (38)$$

the Coulomb parameter and $f_{\alpha n q m}^{(J)}$ the scattering amplitude.

The differential cross section for the charge transfer process (33) in the center of mass system is given by

$$\begin{aligned} \frac{d\sigma_{nlm}}{d\Omega} = & \pi \frac{\mu_A k_{Bn}}{\mu_B k_{A1}} (1 + \delta_{0m}) \left| \sum_{J=0}^{\infty} \sqrt{2J+1} \sum_{m'=0}^l Y_{Jm'}(\Theta, 0) d_{mm'}^{l(+)}(\Theta) \right. \\ & \times \left. \sum_{q=0}^{n-m'-1} \langle nqm' | nlm' \rangle f_{Bnqm'}^{(J)} \right|^2, \end{aligned} \quad (39)$$

where Θ is the scattering angle, $Y_{Jm}(\Theta, \Phi)$ the spherical harmonics, and

$$d_{mm'}^{l(\pm)}(\Theta) = \frac{(-)^{m+m'}}{\sqrt{(1+\delta_{0m})(1+\delta_{0m'})}} [D_{m,m'}^l(0, \Theta, 0) \pm (-)^{m'} D_{m,-m'}^l(0, \Theta, 0)]. \quad (40)$$

The DAO function $\psi_{Bn\nu}(\tau_B, R_B)$ given by Eq. (13) becomes, in the limit $R_B \rightarrow \infty$, the hydrogenic wave function in the parabolic coordinates. The overlap integral of this wave function with that in the spherical coordinates is denoted by $\langle nqm | nlm \rangle$ in Eq. (39). Integrating over Θ and summing over m , we obtain the total cross section σ_{nl} for the transfer to $\text{He}^+(nl)$ in the form

$$\sigma_{nl} = \sum_{J=0}^{\infty} \sigma_{nl}^{(J)} \quad (41)$$

with

$$\sigma_{nl}^{(J)} = 4\pi \frac{\mu_A k_{Bn}}{\mu_B k_{A1}} (2J+1) \sum_{m=0}^l \left| \sum_{q=0}^{n-m-1} \langle nqm | nlm \rangle f_{Bnqm}^{(J)} \right|^2. \quad (42)$$

We have solved the coupled differential equations (31) numerically by Runge-Kutta-Gill method. For $r \leq 75$, the coupling matrices $S^{(t)}(r)$, $P^{(t)}(r)$ and $U^{(t)}(r)$ of Eq. (27) are calculated by numerical integration over ξ_{α} and η_{α} , and then $\bar{S}^{(l)}(r)$, $\bar{P}^{(l)}(r)$ and $\bar{U}^{(l)}(r)$ are obtained by successive numerical differentiation of them with respect to r . For $r > 75$, we use the following asymptotic expansion for $P(r)$ and $U(r)$,

$$P_{\alpha\nu,\alpha'n'\nu'}(r) \rightarrow \delta_{\alpha\alpha'}\delta_{mm'} \sum_{k=2}^4 \frac{1}{r^k} p_{\alpha\nu,\alpha'n'\nu'}^{(k)} \quad (43)$$

and

$$U_{\alpha\nu,\alpha'n'\nu'}(r) \rightarrow \delta_{\alpha\alpha'}\delta_{nn'}\delta_{\nu\nu'} \left(-k_{\alpha n}^2 + \frac{2k_{\alpha n}\zeta_{\alpha n}}{r} + \frac{J(J+1)}{r^2} \right) + \delta_{\alpha\alpha'} \sum_{k=2}^4 \frac{1}{r^k} \left(\delta_{mm'} u_{\alpha\nu,\alpha'n'\nu'}^{(k)} + \Lambda_{mm'}^{(Jp)} b_{\alpha\nu,\alpha'n'\nu'}^{(k)} \right), \quad (44)$$

where

$$\Lambda_{mm'}^{(Jp)} = \delta_{m',m+1} \sqrt{[1 + p(-)^J \delta_{0m}](J+m+1)(J-m)} + \delta_{m',m-1} \sqrt{[1 + p(-)^J \delta_{1m}](J-m+1)(J+m)}. \quad (45)$$

Coefficients $p_{\alpha\nu,\alpha'n'\nu'}^{(k)}$, $u_{\alpha\nu,\alpha'n'\nu'}^{(k)}$ and $b_{\alpha\nu,\alpha'n'\nu'}^{(k)}$ appearing in Eqs. (43) and (44), which are obtained exactly by the method of Coulson *et al.* [4], are listed in Table II.

The squared moduli, $|f_{Bnqm}^{(J)}|^2$, of the partial wave amplitudes are tabulated in Table III against both the number of iteration L and the order of the highest derivative T retained in Eq. (22). We see that the iteration converges rapidly and $L = 3$ is enough for both $E_i = 20$ and 200 eV. As for the convergence of the Taylor's expansion (22), $T = 1$ for $E_i = 20$ eV and $T = 2$ for $E_i = 200$ eV are necessary. This is reasonable because Eq. (22) can be interpreted as an expansion in powers of the velocity ratio v/v_e .

Cross sections for charge transfer to all states of $\text{He}^+(n=2)$ are shown in Fig. 3. Solid curve ($E_i < 200$ eV) is the result of the present DAO calculation and the dashed curve ($E_i > 200$ eV) is the result of the semiclassical calculation of Winter and Hatton [5]. In the latter calculation, the electronic wave function is expanded in terms of four molecular orbitals, that correspond to our DAO, with the plane wave electron translation factors(ETF's). Therefore it is the semiclassical limit of the present DAO calculations. The results from the two calculations differ only by about

10% at 200 eV (see also Table IV) and the two curves indicate that they would merge into each other at a slightly higher energy. Solid squares in this figure are the results of the quantum mechanical calculation of Hermet *et al.* [6] where the total wave function is expanded in the same four MO's with ETF of Vaaben-Taulbjerg type.

Partial wave cross sections $\sigma^{(J)} = \sigma_{2S}^{(J)} + \sigma_{2P}^{(J)}$ at $E_i = 200$ eV are plotted in Fig. 4 for the sake of more detailed comparison between the quantal DAO result and its semiclassical limit. In the semiclassical calculation, the transition probability $P(\rho)$ is given as a function of the impact parameter ρ . We have made the comparison by defining the semiclassical partial wave cross section as

$$\sigma^{(J)} = \frac{2\pi}{k_{A1}} \rho P(\rho) \quad \text{with} \quad \rho = J/k_{A1}. \quad (46)$$

The DAO result (solid curve) and the semiclassical result (dashed curve) agree reasonably well each other.

The present DAO results for charge transfer to ${}^4\text{He}^+(2S)$ and ${}^4\text{He}^+(2P)$ are tabulated in Table IV. Results of Winter and Hatton at $E_i = 200$ eV are also shown in this table.

We have also carried out a full quantal calculation using the 4-state MO expansion. This is possible because no spurious coupling terms appear between states with the same principal quantum number n in the separated atom limit. As expected, the results at $E_i = 20$ eV agree very well with DAO results including the partial wave cross sections $\sigma^{(J)}$.

In summary, we have described in detail the distorted atomic orbital expansion method for low energy ion-atom collisions. Though this method is free from the difficulty of spurious couplings, cross sections are determined by solving a set of coupled integro-differential equations instead of differential equations. In order to solve these equations numerically, we have developed an iterative method that reduces

them to a set of second order differential equations. As a numerical example, we have applied this method to $\text{He}^{2+} + \text{H}$ collisions for incident energy $E_i \leq 200$ eV. The iterative method converges fast and the calculated cross section connects naturally to those obtained from a semiclassical calculation for $E_i \geq 200$ eV.

APPENDIX

We give in this appendix explicit formulas to calculate the matrices $S^{(t)}$, $P^{(t)}$ and $U^{(t)}$ defined by Eq. (27). The operators \hat{P}_α and \hat{U}_α in Eqs. (24) and (27) are defined by

$$\hat{P}_\alpha = -\frac{\partial}{\partial R_\alpha} + \frac{1}{R_\alpha} \hat{q}_\alpha \quad (\text{A1})$$

$$\begin{aligned} \hat{U}_\alpha = & 2\mu_\alpha \left(\frac{m_\alpha}{2} \Delta_\alpha - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R} - E \right) + \frac{\mathbf{J}^2 - 2J_{\alpha z}^2}{R_\alpha^2} \\ & - \frac{\partial^2}{\partial R_\alpha^2} + \frac{2}{R_\alpha} \hat{q}_\alpha \frac{\partial}{\partial R_\alpha} - \frac{(\xi_\alpha - \kappa_\alpha \eta_\alpha)^2}{4} \Delta_\alpha - \frac{\hat{B}_\alpha}{R_\alpha^2}, \end{aligned} \quad (\text{A2})$$

where

$$\hat{B}_\alpha = [\mathcal{L}_\alpha - s_\alpha(J_{\alpha z} - 1)]J_{\alpha-} + [-\mathcal{L}_\alpha - s_\alpha(J_{\alpha z} + 1)]J_{\alpha+} \quad (\text{A3})$$

is the Coriolis interaction. \mathbf{J} is the total angular momentum operator, and $J_{\alpha z}$ and $J_{\alpha\pm}$ are the $\hat{\mathbf{R}}_\alpha$ -component and spherical component of \mathbf{J} , respectively.

$$J_{\alpha z} = -i \frac{\partial}{\partial \phi_\alpha} \quad (\text{A4})$$

$$J_{\alpha\pm} = e^{\mp i \phi_\alpha} \left(\frac{i}{\sin \Theta_\alpha} \frac{\partial}{\partial \Phi_\alpha} \pm \frac{\partial}{\partial \Theta_\alpha} - i \cot \Theta_\alpha \frac{\partial}{\partial \phi_\alpha} \right) \quad (\text{A5})$$

Other operators in Eqs. (A1), (A2) and (A3) are defined by

$$\hat{q}_\alpha = \frac{1}{\xi_\alpha + \kappa_\alpha \eta_\alpha} \left[(\xi_\alpha^2 - 1) \frac{\partial}{\partial \xi_\alpha} - \kappa_\alpha (1 - \eta_\alpha^2) \frac{\partial}{\partial \eta_\alpha} \right] \quad (\text{A6})$$

$$\Delta_\alpha = \frac{4}{R_\alpha^2(\xi_\alpha^2 - \eta_\alpha^2)} \left[\frac{\partial}{\partial \xi_\alpha} (\xi_\alpha^2 - 1) \frac{\partial}{\partial \xi_\alpha} + \frac{\partial}{\partial \eta_\alpha} (1 - \eta_\alpha^2) \frac{\partial}{\partial \eta_\alpha} \right] - \frac{4J_{\alpha z}^2}{R_\alpha^2(\xi_\alpha^2 - 1)(1 - \eta_\alpha^2)} \quad (\text{A7})$$

$$\mathcal{L}_\alpha = \frac{\sqrt{(\xi_\alpha^2 - 1)(1 - \eta_\alpha^2)}}{\xi_\alpha + \kappa_\alpha \eta_\alpha} \left(-\kappa_\alpha \frac{\partial}{\partial \xi_\alpha} - \frac{\partial}{\partial \eta_\alpha} \right) \quad (\text{A8})$$

$$s_\alpha = \frac{\xi_\alpha \eta_\alpha - \kappa_\alpha}{\sqrt{(\xi_\alpha^2 - 1)(1 - \eta_\alpha^2)}} \quad (\text{A9})$$

$$\kappa_\alpha = \begin{cases} -1 & (\alpha = A) \\ +1 & (\alpha = B) \end{cases} \quad (\text{A10})$$

Independent variables are R_α , ξ_α , η_α , ϕ_α , Θ_α and Φ_α in all the above expressions. When \hat{P}_α and \hat{U}_α operate on DAO basis function (17), \hat{B}_α is the only operator that changes the angular part $\mathcal{D}_m^{JM p}(\phi_\alpha, \Theta_\alpha, \Phi_\alpha)$,

$$\begin{aligned} \hat{B}_\alpha \psi_{\alpha n q m}^{JM p} &= \Lambda_{m, m+1}^{(J p)} (\mathcal{L}_\alpha - m s_\alpha) \psi_{\alpha n q m}(\xi_\alpha, \eta_\alpha; R_\alpha) \mathcal{D}_{m+1}^{JM p}(\phi_\alpha, \Theta_\alpha, \Phi_\alpha) \\ &+ (1 - \delta_{0m}) \Lambda_{m, m-1}^{(J p)} (-\mathcal{L}_\alpha - m s_\alpha) \psi_{\alpha n q m}(\xi_\alpha, \eta_\alpha; R_\alpha) \mathcal{D}_{m-1}^{JM p}(\phi_\alpha, \Theta_\alpha, \Phi_\alpha). \end{aligned} \quad (\text{A11})$$

Matrices $S^{(t)}$, $P^{(t)}$ and $U^{(t)}$ can be calculated by numerical integration over ξ_α and η_α after using the following formula for the overlap integral of the angular function $\mathcal{D}_m^{JM p}(\phi_\alpha, \Theta_\alpha, \Phi_\alpha)$ between different arrangement channels.

$$\begin{aligned} &\int d\hat{R}_A d\phi_A [\mathcal{D}_m^{JM p}(\phi_A, \Theta_A, \Phi_A)]^* \mathcal{D}_{m'}^{JM p}(\phi_B, \Theta_B, \Phi_B) \\ &= \frac{(-)^{m'+m}}{\sqrt{(1 + \delta_{0m'})(1 + \delta_{0m})}} [D_{m', m}^J(0, \theta, 0) + p(-)^{J+m} D_{m', -m}^J(0, \theta, 0)], \end{aligned} \quad (\text{A12})$$

where θ is the angle between \mathbf{R}_A and \mathbf{R}_B .

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FIGURES

FIG. 1. Jacobi coordinates $(\mathbf{R}_A, \mathbf{r}_A)$ and $(\mathbf{R}_B, \mathbf{r}_B)$.

FIG. 2. Schematic energy spectra of h_A and h_B . Solid lines are those included in the basis sets $\{\psi_{An\nu}, \psi_{Bn'\nu'}\}$ and dashed lines are those not included.

FIG. 3. Charge transfer cross sections, $\sigma_{2S} + \sigma_{2P}$. Solid curve: the result of the present DAO calculation. Dashed curve: the result of the semiclassical calculation by Winter and Hatton [5] using the MO's with plane wave ETF's . Solid squares: the result of the quantum mechanical calculation by Hemert *et al.* [6] using the MO's with Vaaben-Taulbjerg type ETF's.

FIG. 4. J-dependence of charge transfer cross section, $\sigma^{(J)} = \sigma_{2S}^{(J)} + \sigma_{2P}^{(J)}$. Solid curve: the result of the present DAO calculation. Dashed curve: the result of the semiclassical calculation by Winter and Hatton [5] using the MO's with plane wave ETF's .

TABLES

TABLE I. DAO's used in the present calculation. The united atom designation of the corresponding MO-limit is shown in the third column.

Arrangement	Separated atom	United atom
Channel	(α, n, q, m)	
H + ${}^4\text{He}^{2+}$	$(A, 1, 0, 0)$	$2p\sigma$
H ⁺ + ${}^4\text{He}^+$	$(B, 2, 0, 0)$	$3d\sigma$
	$(B, 2, 1, 0)$	$2s\sigma$
	$(B, 2, 0, 1)$	$2p\pi$

TABLE II. Asymptotic expansion coefficients, $p_{\alpha\nu,\alpha'n'\nu'}^{(k)}$, $u_{\alpha\nu,\alpha'n'\nu'}^{(k)}$ and $b_{\alpha\nu,\alpha'n'\nu'}^{(k)}$, of the coupling terms $P(r)$ and $U(r)$, in Eqs. (43) and (44). Channels are denoted by united atom designation of the corresponding MO-limit (see Table I).

Channel		k		
$\alpha\nu$	$\alpha'n'\nu'$	2	3	4
		$p_{\alpha\nu,\alpha'n'\nu'}^{(k)}$		
$3d\sigma$	$2s\sigma$	0.5000	1.0004	-0.5000
		$u_{\alpha\nu,\alpha'n'\nu'}^{(k)}$		
$2p\sigma$	$2p\sigma$	0.0000	0.0000	-26459
$3d\sigma$	$3d\sigma$	-4401.0	-4399.8	-17612
$2s\sigma$	$2s\sigma$	4403.0	-4401.8	-13214
$2p\pi$	$2p\pi$	0.0000	4400.8	-14312
$3d\sigma$	$2s\sigma$	-1.0000	-2.2068	-2.5012
		$b_{\alpha\nu,\alpha'n'\nu'}^{(k)}$		
$3d\sigma$	$2p\pi$	1.0000	0.5000	0.3752
$2s\sigma$	$2p\pi$	-1.0000	0.5000	0.6252

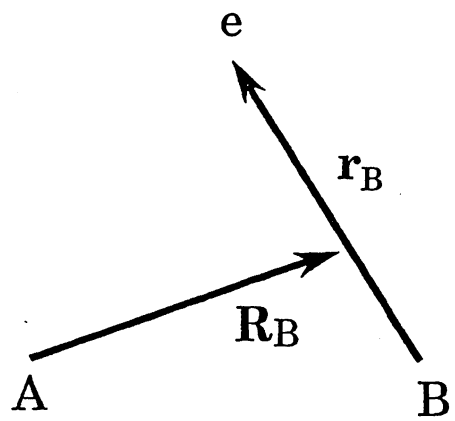
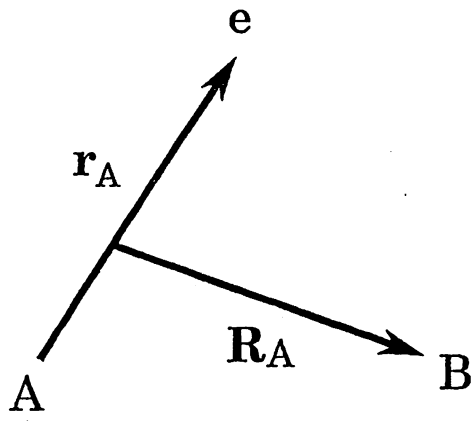
TABLE III. Convergence in L and T of the squared moduli of the partial wave amplitude, $|f_{Bnqm}^{(J)}|^2$. Channels are denoted by united atom designation of the corresponding MO-limit (see Table I). Numbers in square brackets are powers of 10.

T	L	Channel		
		$3d\sigma$	$2s\sigma$	$2p\sigma$
$E_i = 20 \text{ eV}, J = 100$				
0	0	1.15[-13]	1.50[-17]	1.41[-15]
1	1	1.38[-13]	2.10[-17]	1.71[-15]
	2	1.39[-13]	2.13[-17]	1.72[-15]
	3	1.39[-13]	2.13[-17]	1.72[-15]
2	1	1.38[-13]	2.11[-17]	1.71[-15]
	2	1.38[-13]	2.15[-17]	1.72[-15]
	3	1.38[-13]	2.15[-17]	1.72[-15]
$E_i = 200 \text{ eV}, J = 400$				
0	0	2.67[-08]	1.25[-10]	1.33[-09]
1	1	4.41[-08]	2.34[-10]	2.14[-09]
	2	4.50[-08]	2.42[-10]	2.18[-09]
	3	4.51[-08]	2.42[-10]	2.18[-09]
2	1	4.65[-08]	2.36[-10]	2.16[-09]
	2	4.75[-08]	2.45[-10]	2.20[-09]
	3	4.75[-08]	2.45[-10]	2.20[-09]

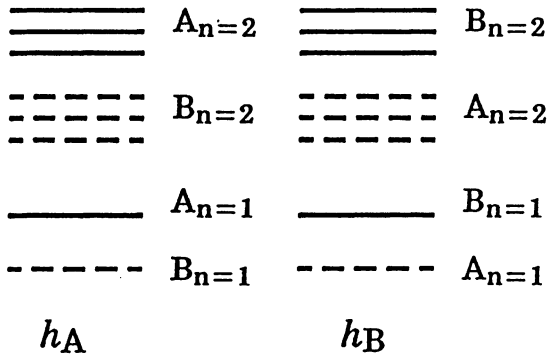
TABLE IV. Charge transfer cross section, σ_{nl} , in units of 10^{-16}cm^2 . Numbers in square brackets are powers of 10.

$E_i(\text{eV})$	Method	σ_{2S}	σ_{2P}	$\sigma_{2S} + \sigma_{2P}$
20	DAO	3.5 [-9]	3.6 [-9]	7.1 [-9]
50	DAO	1.5 [-5]	6.4 [-5]	7.9 [-5]
100	DAO	0.13[-2]	3.2 [-2]	3.3 [-2]
200	DAO	0.03	0.21	0.24
	WH ^a	0.041	0.227	0.268

^aReference [5].



$$Z_A = Z_B$$



$$Z_A = 1, Z_B = 2$$

