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SPIN EXCHANGE IN COLLISIONS BETWEEN He^+ IONS

G. M. RESSLER
F. G. MAJOR

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GSFC — GODDARD SPACE FLIGHT CENTER —
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ABSTRACT

The spin exchange cross section for the collision between two He^+ ions is calculated in the impact parameter approximation with the use of a variational technique to determine the He^+ - He^+ interaction potential due to exchange. It is found that the spin exchange cross section reaches a maximum of $3.66\ \pi\ a_0^2$ at a relative impact energy of 85 e.v. and falls rapidly to zero below 10 e.v. As applied to a proposed ionic frequency standard, the results indicate that relaxation effects due to spin exchange are negligibly small.

SPIN EXCHANGE IN COLLISIONS BETWEEN He^+ IONS

INTRODUCTION

The use of $(Hg^{199})^+$ ions confined in an RF quadrupole field as the atomic reference system in a highly stable atomic frequency standard has recently been proposed by F. G. Major.[1] With this system, an accuracy of one part in 10^{13} and a fractional line width of 10^{-11} at the microwave resonance frequency of 40.74 GHz are predicted.

The basic feature which limits the reproducibility and stability of an atomic frequency standard is the degree to which the reference atoms can be localized in a perturbation free environment. The standards which exist today, e.g., Cesium, Rubidium and Hydrogen Maser, basically differ only in the amount and manner of isolation of these atoms.

In the hydrogen maser, which is presently the most stable atomic frequency standard, all external perturbations have been reduced to a point where spin exchange between the reference hydrogen atoms themselves is essentially the only perturbation which limits its short term stability. For a hydrogen maser operating at a typical temperature of 300°K, which corresponds to a relative impact energy of $\sim .04$ e.v., the spin exchange cross section between hydrogen atoms is about $30\,\pi a_0^2$.[2,3]

It has been shown[1] that the external perturbations associated with the proposed $(Hg^{199})^+$ ionic frequency standard should, as in the case of the hydrogen maser, be negligible. However, there are two important perturbations which arise from the mutual interaction of the confined particles, whose effects have yet to be discussed in any detail. These are the Stark effect due to the interaction of the electric field of one ion with another, and spin exchange between the unpaired electrons of the ions. It is with respect to the latter that this paper will be devoted. A treatment of the Stark effect will be attempted at a later date.

Spin exchange as a relaxation process leading to frequency shifts was first considered by Purcell and Field[4] and Wittke and Dicke[5]. Basically, the spin exchange process is as follows:

In a collision between two, spin 1/2, particles there will be a finite probability that the spin of one particle is exchanged with that of the other. If α denotes the "spin up" state and β the "spin down" state, then there are three possible symmetric combinations with respect to the exchange

$$\alpha(1)\,\alpha(2),$$

$$\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)],$$

$$\beta(1)\,\beta(2),$$

and one possible antisymmetric combination

$$\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]\,.$$

The former are called the triplet and correspond to total spin $S = 1$; the latter is called the singlet and corresponds to $S = 0$. Now, assuming the particles initially have opposite spins, then the state

$$\psi(\text{initial}) = \alpha(1)\,\beta(2)$$

may be represented by an equal mixture of symmetric and antisymmetric parts, thus

$$\psi(\text{initial}) = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)]\right\} + \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]\right\}.$$

During the collision this state may be changed such that the final state is no longer an equal mixture of symmetries, i.e.,

$$\psi(\text{final}) = A\left\{\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)]\right\} + B\left\{\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]\right\}$$

or

$$\psi(\text{final}) = \frac{A+B}{\sqrt{2}}\,\alpha(1)\,\beta(2) + \frac{A-B}{\sqrt{2}}\,\alpha(2)\,\beta(1).$$

Therefore, after the collision, there is a finite probability

$$p = \left| \frac{A - B}{\sqrt{2}} \right|^2$$

that the particles will be in the "spin exchanged" state $\alpha(2)\,\beta(1)$.

The problem of the interaction of two complex ions such as $(Hg^{199})^+$ would be extremely difficult to solve. Therefore, in order to make the problem tractable while maintaining the basic properties of the actual system of interest, the theoretical treatment will be directed to the interaction between two He^+ ions. If only the shielding effects of the electrons in the closed shells of $(Hg^{199})^+$ are considered, then both $(Hg^{199})^+$ and He^+ can be considered as hydrogenic ions differing only in their size and mass.

The theoretical treatment of the collision will be "semi-classical," that is, the He^+ ions are considered to move adiabatically along classical trajectories and time-dependent perturbation theory is used to determine the resulting effects on the electron wave functions (Impact Parameter Treatment).

COLLISION THEORY[6,7]

If it is assumed that the interaction potential which determines the trajectory of the He^+ ions is purely Coulomb (e^2/R), the ions may be thought of as moving along classical orbits (diffraction effects will be small) when[8]

$$\left(\frac{\lambda\!\!\!^{-}}{R_c}\right)^{1/2} << 1 , \tag{1}$$

where $\lambda\!\!\!^{-}$ is the free particle wavelength divided by 2π and R_c is the distance of closest approach of the ions. In terms of the relative impact energy E (e.v.) in the center of mass of the He^+ - He^+ system, condition (1) can be written as

$$6.69 \times 10^{-2} E^{1/4} << 1$$

which will be satisfied for impact energies up to about 1000 e.v.

The collision may also be treated as adiabatic (slow) if

$$\frac{\Delta E}{\hbar} \tau_c >> 1 , \tag{2}$$

where ΔE is the exitation energy for a transition from the ground state to the first excited state and τ_c is the total time of the collision. (It is assumed that the He^+ ions are initially in the ground state.) For the He^+ - He^+ system condition (2) becomes

$$4.03 \times 10^{-6} E^{3/2} << 1$$

which is also satisfied for energies up to about 1000 e.v.

In summary, for E < 1000 e.v. the ions can be thought of as moving adiabatically along classical trajectories and time-dependent perturbation theory can be used to determine the probability of a spin exchange occurring.

Since the collision is adiabatic, the internuclear distance can be treated as a slowly varying function of time, and the He^+ - He^+ system may be thought of, at each instant of time, as an He_2^{++} molecule with fixed nuclei. The total molecular wave function $\psi(r_1 s_1, r_2 s_2, R(t))$ is a solution of the time dependent Schrödinger equation

$$\mathcal{H}\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}, \tag{3}$$

where the Hamiltonian $\mathcal{H}$ is given by

$$\begin{aligned}\mathcal{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{2}\nabla_i^2 - \frac{\hbar^2}{2M}\nabla_R^2 + \frac{Z^2e^2}{R(t)} + \frac{e^2}{r_{12}}\\ - Ze^2\sum_{i=1}^{2}\left[\frac{1}{|\underline{r}_i - \underline{R}_A(t)|} + \frac{1}{|\underline{r}_i - \underline{R}_B(t)|}\right],\end{aligned} \tag{4}$$

and where (see Figure 1), in the center of mass of the nuclei; r_{12} is the interelectronic distance; R is the internuclear distance; r_1, r_2 and R_A, R_B are respectively the coordinates of the electrons and nuclei of the molecule; m is the electronic mass; M is the reduced mass of the nuclei; s_1, s_2 are the z components of the electron spins.

A solution of (3) is

$$\begin{aligned}\Psi(r_1 s_1, r_2 s_2, R(t)) = C_+(R(t))X_-(s_1, s_2)\,\Phi_+(r_1, r_2, R(t))\,e^{-\frac{i}{\hbar}\int^t V_+(R(t))dt}\\ + C_-(R(t))X_+(s_1, s_2)\Phi_-(r_1, r_2, R(t))\,e^{-\frac{i}{\hbar}\int^t V_-(R(t))dt}\end{aligned} \tag{5}$$

where the spatial wave functions Φ_+ and Φ_- are, at each instant of time, solutions of the stationary state Schrödinger equation

$$H\Phi_\pm = V_\pm\,\Phi_\pm\ , \tag{6}$$

with H defined by

$$H = \mathcal{H} + \frac{\hbar^2}{2M}\nabla_R^2 .$$

The eigenvalues $V_+(R(t))$ and $V_-(R(t))$ of equation (6) are the interaction potentials of the molecule in the triplet and singlet states respectively, and are determined by a variational method which is described later.

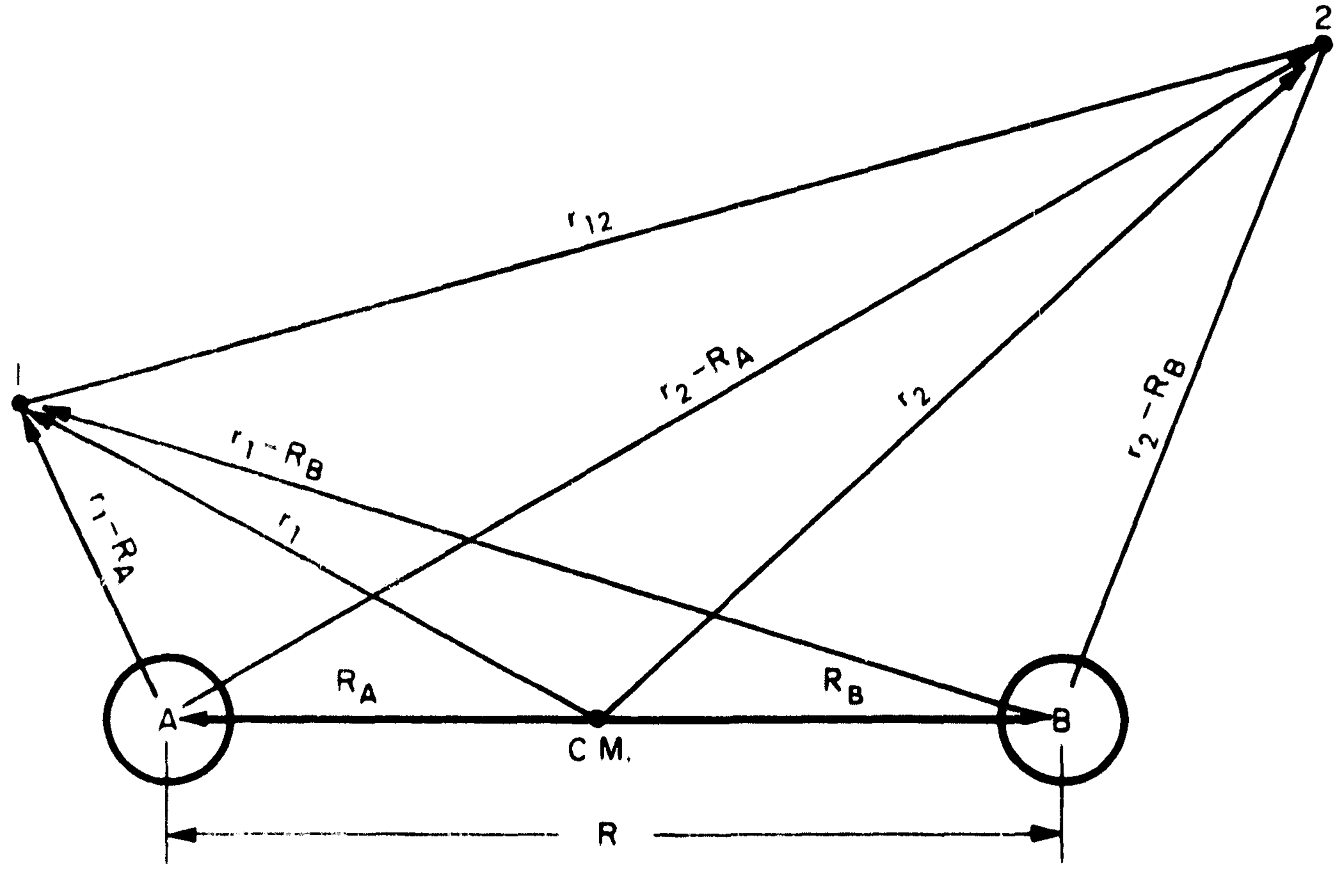

Figure 1. Coordinate System for Impact Parameter Treatment

For large R the states Φ_+ and Φ_- behave as

$$\Phi_\pm \to [\phi(A1)\,\phi(B2) \pm \phi(A2)\,\phi(B1)],$$

where ϕ (A1), ϕ(B2) are the wave functions of the ions at $R = \infty$ and ϕ (A2), ϕ (B1) are the wave functions representing the exchange of the spatial coordinates of the electrons. In the limit as $R \to \infty$ the exchange terms vanish and

$$\Phi_+ = \Phi_- = \phi(A1)\,\phi(B2).$$

The functions X_+ and X_- are respectively the triplet and singlet spin wave functions given by

$$X_+ = \begin{cases} \alpha(1)\,\alpha(2) \\ \frac{1}{\sqrt{2}}\,[\alpha(1)\,\alpha(2) + \alpha(2)\,\beta(1)] \\ \beta(1)\,\beta(2) \end{cases}$$

and

$$X_- = \frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)],$$

where as before $\alpha(1)$ denotes electron 1 in the "spin up" state, $\beta(2)$ denotes electron 2 in the "spin down" state, etc.

It should be noted that the products $X_+ \Phi_-$ and $X_- \Phi_+$ which correspond to the $^3\Sigma_u^+$ and $^1\Sigma_g^+$ states of the molecule respectively are, as required by the Pauli Principle, antisymmetric with respect to an exchange of both the space and spin coordinates, making the total molecular wave function antisymmetric in the same exchange.

If at time $t = -\infty$ the system is chosen to be in the initial state

$$\psi(-\infty) = \alpha(1)\,\beta(2)\,\phi(A1)\,\phi(B2) = \frac{1}{\sqrt{2}}(X_+ + X_-)\,\phi(A1)\,\phi(B2), \tag{7}$$

where specifically

$$X_+ = \frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)]$$

(an initial state represented by $X_+ = \alpha(1)\,\alpha(2)$ or $X_+ = \beta(1)\,\beta(2)$ will not lead to a spin exchange), then the coefficients C_+ and C_- of equation (5) are given by

$$C_+(R(t)) = \frac{1}{\sqrt{2}} e^{\frac{i}{\hbar}\int^{-\infty} V_+(R(t))dt} \tag{8}$$

and

$$C_-(R(t)) = \frac{1}{\sqrt{2}} e^{\frac{i}{\hbar}\int^{-\infty} V_-(R(t))\,dt}, \tag{9}$$

where $C_+(t) = 1/\sqrt{2}$ and $|C_+|^2 + |C_-|^2 = 1$.

Substituting (8) and (9) into (5) gives the adiabatic time-dependent molecular wave function for arbitrary t

$$\Psi(r_1 s_1, r_2 s_2, R(t)) = \frac{1}{\sqrt{2}} \Big[X_-(s_1, s_2)\, \Phi_+(r_1, r_2, R(t))\, e^{-\frac{i}{\hbar}\int_{-\infty}^{t} V_+(R(t))\,dt} + X_+(s_1, s_2)\, \Phi_-(r_1, r_2, R(t))\, e^{-\frac{i}{\hbar}\int_{-\infty}^{t} V_-(R(t))\,dt} \Big]. \tag{10}$$

Now, the spin exchange operator P_{ex} is such that

$$\alpha(2)\,\beta(1) = P_{ex}\,\alpha(1)\,\beta(2).$$

Therefore, if the system was in an initial state given by (7) the final spin exchanged state would be

$$\psi(+\infty) = P_{ex}\,\psi(-\infty)$$

or

$$\psi(+\infty) = \alpha(2)\,\beta(1)\,\phi(A1)\,\phi(B2) = \frac{1}{\sqrt{2}}(X_+ - X_-)\,\phi(A1)\,\phi(B2). \tag{11}$$

The probability p that the system would be found in the particular state $\psi(+\infty)$, i.e., the probability that a spin exchange has occurred after the collision, is given by the squared modulus of the projection of $\psi(+\infty)$ on $\Psi(+\infty)$; thus

$$p = |\langle \psi(+\infty) \mid \Psi(+\infty) \rangle|^2. \tag{12}$$

Using the fact that at $t = +\infty$, $\Phi_+ = \Phi_- = \phi(A1)\,\phi(B2)$ equation (10) becomes

$$\Psi(+\infty) = \frac{1}{\sqrt{2}} \left[X_- \phi(A1)\, \phi(B2)\, e^{-\frac{i}{\hbar}\int_{-\infty}^{+\infty} V_+ \, dt} \right.$$

$$\left. + X_+ \phi(A1)\, \phi(B2)\, e^{-\frac{i}{\hbar}\int_{-\infty}^{+\infty} V_- \, dt} \right] \tag{13}$$

Hence, from equations (11), (12), and (13)

$$p = \left| \frac{1}{2} \left(e^{-\frac{i}{\hbar}\int_{-\infty}^{+\infty} V_- \, dt} - e^{-\frac{i}{\hbar}\int_{-\infty}^{+\infty} V_+ \, dt} \right) \right|^2 , \tag{14}$$

where the conditions

$$\langle X_\pm \mid X_\mp \rangle = 0, \quad \langle X_\pm \mid X_\pm \rangle = 1$$

and

$$\langle \phi(A1) \mid \phi(A1) \rangle = \langle \phi(B2) \mid \phi(B2) \rangle = 1$$

were used.

Thus, the probability that the system will go from the initial state given by equation (7), to the final state given by equation (11), i.e., the probability that a spin exchange has occurred, is from equation (14)

$$p = \mathrm{Sin}^2 \frac{\gamma}{2} , \tag{15}$$

where

$$\gamma = \frac{1}{\hbar} \int_{-\infty}^{+\infty} (V_+ - V_-)\, dt . \tag{16}$$

Now, the classical trajectory along which the ions move is assumed to be determinated only by the Coulomb interaction, therefore, from classical orbit theory[9]

$$dt = \left(\frac{M}{2}\right)^{1/2} \frac{dR}{\left[E\left(1 - \frac{b^2}{R^2}\right) - \frac{e^2}{R}\right]^{1/2}}, \tag{17}$$

where b is the classical impact parameter. Using (17) in (16) gives

$$\gamma = \frac{1}{\hbar}\left(\frac{M}{2}\right)^{1/2} \int_{R(t=-\infty)}^{R(t=+\infty)} \frac{(V_+ - V_-)\, dR}{\left[E\left(1 - \frac{b^2}{R^2}\right) - \frac{e^2}{R}\right]^{1/2}}. \tag{18}$$

However, the orbit is symmetrical about the distance of closest approach of the ions R_c (classical turning point), which allows (18) to be written as

$$\gamma = \left(\frac{2M}{\hbar^2}\right)^{1/2} \int_{R_c}^{+\infty} \frac{(V_+ - V_-)\, dR}{\left[E\left(1 - \frac{b^2}{R^2}\right) - \frac{e^2}{R}\right]^{1/2}}, \tag{19}$$

with

$$R_c = \frac{e^2}{2E} + \frac{1}{2}\left[\frac{e^4}{E^2} + 4b^2\right]^{1/2} \tag{20}$$

The differential cross section for scattering with spin exchange is

$$d\sigma_{ex} = p\, d\sigma_c, \tag{21}$$

where p, the probability that a spin exchange has occurred during the collision, is defined by equation (15) and where (see Figure 2) $d\sigma_c$ is the (elastic) differential cross section for classical scattering

$$d\sigma_c = 2\pi b\, db. \tag{22}$$

Substitution (22) and (15) in (21) and then integrating over the impact parameter b, leads to the total cross section for spin exchange

$$\sigma_{ex} = 2\pi \int_0^{\infty} b \, \mathrm{Sin}^2 \left(\frac{\gamma}{2}\right) db, \tag{23}$$

with γ defined by equations (19) and (20).

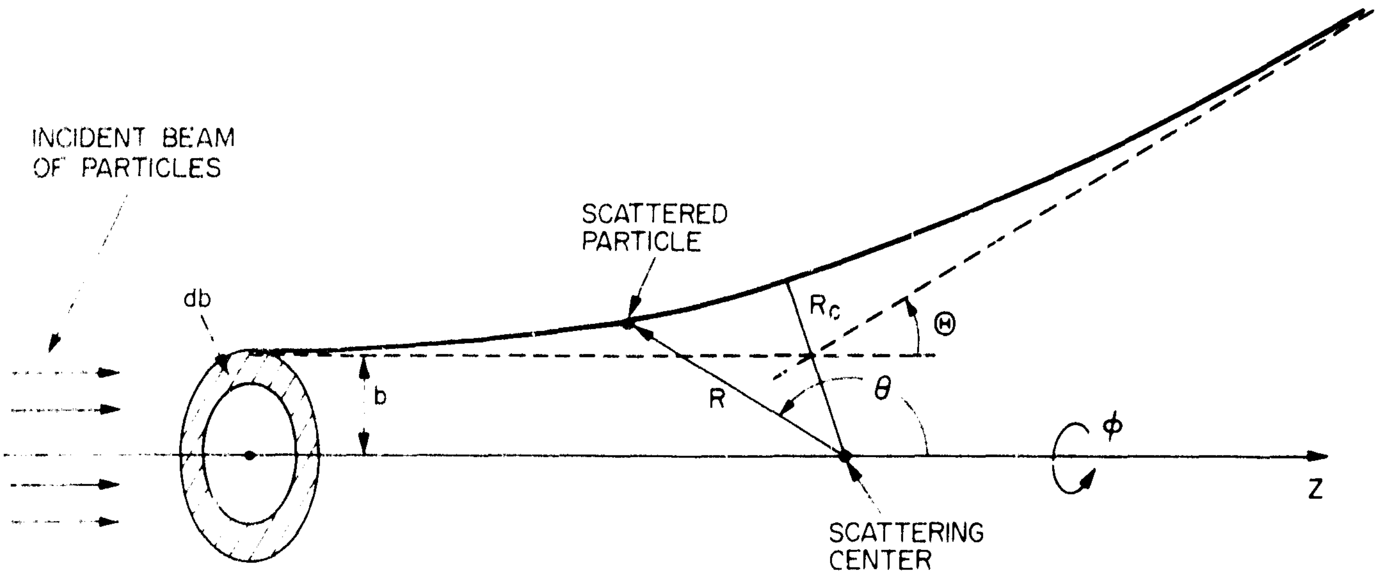

Figure 2. Classical scattering of a particle in a central field; b is the impact parameter, R_c is the distance of closest approach, R and θ are the instantaneous coordinates of the particle, Θ is the scattering angle and ϕ is the azimuthal angle.

EXCHANGE INTERACTION

The He^+ - He^+ exchange interaction potentials V_+ and V_- were evaluated by adapting a method used by Rosen[10, 11] for determining the normal state $({}^1\Sigma_g^+)$ of the hydrogen molecule.

If it is assumed that the He_2^+ ions form an He_2^{++} molecule with fixed nuclei then the Hamiltonian of the molecule is

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^{2} \nabla_i^2 - Ze^2 \sum_{i=1}^{2} \left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}} \right) + \frac{Z^2 e^2}{R} + \frac{e^2}{r_{12}} ,$$

where (see Figure 3) r_{A1} and r_{A2} are the distances between nucleus A and electrons 1 and 2 respectively, r_{B1} and r_{B2} are the distances between nucleus B and electrons 1 and 2 respectively, and $Z = 2$ is the atomic number for He^+. All other quantities are defined as before.

The properly symmetrized wave function which will be used to represent the molecule [see equation (6)] is

$$\Phi_\pm = \phi(A1)\,\phi(B2) \pm \phi(A2)\,\phi(B1)$$

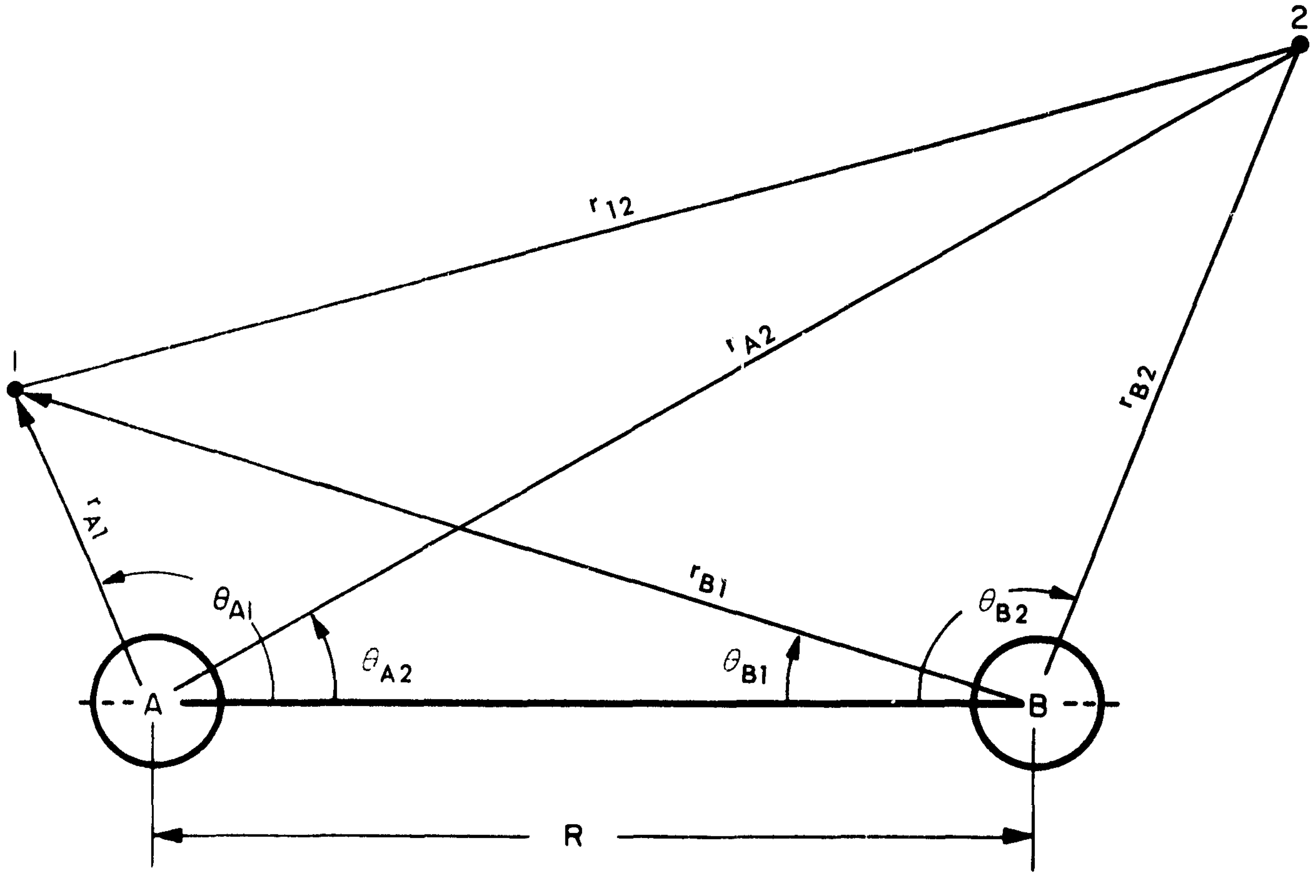

Figure 3. Coordinate system for calculation of He^+ − He^+ exchange potentials.

where again (see page 7), Φ_+ corresponds to the singlet spin case and Φ_- to the triplet.

Now, a basic assumption associated with this calculation is that the electronic charge distribution of one ion is distorted (polarized) by the field due to the charge distribution of the other ion; the distortion increasing as the ions approach each other. To account for this effect, the individual ionic wave functions are written in the form

$$\phi = \phi^0 + \sigma \phi'$$

where ϕ^0 is the ground state wave function of the He$^+$ ion, ϕ' is a function with an angular dependence such that it is symmetrical about the inter-nuclear axis but not in the plane which contains the axis, and σ is a variable parameter which can be thought of as a measure of the distortion.

Specifically, the functions ϕ^0 and ϕ' which are finite at the origin, go to zero at infinity and satisfy the orthonormality conditions

$$\langle \phi^0 | \phi^0 \rangle = \langle \phi' | \phi' \rangle = 1$$

and

$$\langle \phi^0 | \phi' \rangle = \langle \phi' | \phi^0 \rangle = 0,$$

are given by

$$\phi^0(A1) = N_0 \, e^{-\frac{\bar{Z}}{a_0} r_{A1}} ; \quad \phi^0(A2) = N_0 \, e^{-\frac{\bar{Z}}{a_0} r_{A2}} ;$$

$$\phi^0(B1) = N_0 \, e^{-\frac{\bar{Z}}{a_0} r_{B1}} ; \quad \phi^0(B2) = N_0 \, e^{-\frac{\bar{Z}}{a_0} r_{B2}} ;$$

$$\phi'(A1) = N_1 \, e^{-\frac{\bar{Z}}{a_0} r_{A1}} \, r_{A1} \operatorname{Cos} \theta_{A1} ; \quad \phi'(A2) = N_1 \, e^{-\frac{\bar{Z}}{a_0} r_{A2}} \, r_{A2} \operatorname{Cos} \theta_{A2} . \tag{24}$$

$$\phi'(B1) = -N_1 \, e^{-\frac{\bar{Z}}{a_0} r_{B1}} \, r_{B1} \operatorname{Cos} \theta_{B1} ; \quad \phi'(B2) = -N_1 \, e^{-\frac{\bar{Z}}{a_0} r_{B2}} \operatorname{Cos} \theta_{B2} ,$$

where ϕ_{A1}, ϕ_{A2}, ϕ_{B1}, ϕ_{B2} are defined as in Figure 3, $\bar{Z}$ is a variable parameter referred to as the "effective" nuclear charge, a_0 is the first Bohr radius, and by normalization

$$N_0 = \left(\frac{\bar{Z}^3}{\pi a_0^3} \right)^{1/2}, \quad N_1 = \left(\frac{\bar{Z}^5}{\pi a_0^5} \right)^{1/2}.$$

The minus sign in ϕ' (B1) and ϕ' (B2) assures that all the functions of (24) are symmetrical with respect to a plane midway between and perpendicular to the line joining the nuclei.

The functions ϕ^0 all satisfy a wave equation of the form

$$H^0 \phi^0 = \bar{Z}^2 E^0 \phi^0,$$

where

$$H^0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{\bar{Z} e^2}{r}$$

and $E^0 = 13.605$ e.v. is the ground state energy of Hydrogen. The functions ϕ', which represent the 2p state of a hydrogenic atom of charge $2Z$, are solutions of

$$H' \phi' = \bar{Z}^2 E^0 \phi',$$

where

$$H' = -\frac{\hbar^2}{2m} \nabla^2 - \frac{2 \bar{Z} e^2}{r}.$$

Now, in order to evaluate the potentials V_+ and V_-, a variational method is used in which the parameters $\bar{Z}$, and σ are varied so that

$$V_{\pm} = \frac{\langle \Phi_{\mp} | H | \Phi_{\mp} \rangle}{\langle \Phi_{\mp} | \Phi_{\mp} \rangle} \tag{25}$$

is a minimum. The method is as follows. For a particular value of R, a value of $\bar{Z}$ is chosen and σ is then varied until a minimum of (25) is found. Taking this value of σ as fixed, $\bar{Z}$ is then varied until another minimum is reached. This procedure is continued until a minimum is reached with respect to both σ and $\bar{Z}$. (The integrals which are needed in the evaluation of (25) are given in reference 7.)

The results of the minimization for He^+ - He^+ are given in Tables 1 and 2. Plots of V_+, V_- and $(V_+ - V_-)$ are given in Figures 4 and 5 respectively.

Table 1. $\bar{Z}_+$, σ_+, V_+ and $\bar{Z}_-$, σ_-, V_- for various values of R

(V_+ and V_- are in e.v. and R is in units $a_0 = 5.29 \times 10^{-11}$ meter)

R	Z_+	σ_+	V_+	Z_-	σ_-	V_-
0.1	2.65	-0.76	0.9915382D 03	3.57	-0.01	0.8400521D 03
0.2	2.50	-0.60	0.4577075D 03	3.35	0.07	0.3192747D 03
0.3	2.39	-0.48	0.2940353D 03	3.13	0.11	0.1617459D 03
0.4	2.32	-0.38	0.1987872D 03	2.94	0.14	0.9275601D 02
0.5	2.27	-0.30	0.1482373D 03	2.78	0.16	0.5743765D 02
0.6	2.23	-0.24	0.1148298D 03	2.64	0.17	0.3780716D 02
0.7	2.20	-0.19	0.9122249D 02	2.52	0.17	0.2539742D 02
0.8	2.17	-0.14	0.7381676D 02	2.41	0.18	0.1962205D 02
0.9	2.15	-0.10	0.6062741D 02	2.33	0.18	0.1559789D 02
1.0	2.12	-0.07	0.5045272D 02	2.25	0.17	0.1325538D 02
1.1	2.10	-0.04	0.4250392D 02	2.19	0.17	0.1195254D 02
1.2	2.09	-0.02	0.3623637D 02	2.13	0.16	0.1130049D 02
1.3	2.07	-0.01	0.3125602D 02	2.09	0.16	0.1103662D 02
1.4	2.06	0.0	0.2727334D 02	2.05	0.15	0.1099796D 02
1.5	2.05	0.01	0.2406450D 02	2.03	0.14	0.1107139D 02
1.6	2.04	0.02	0.2146301D 02	2.00	0.13	0.1118231D 02
1.7	2.03	0.03	0.1934363D 02	1.99	0.12	0.1128061D 02
1.8	2.03	0.03	0.1759662D 02	1.98	0.11	0.1133791D 02
1.9	2.02	0.03	0.1615172D 02	1.97	0.10	0.1133845D 02
2.0	2.02	0.03	0.1494454D 02	1.97	0.09	0.1127569D 02
2.1	2.02	0.03	0.1392800D 02	1.97	0.08	0.1115410D 02
2.2	2.01	0.03	0.1306258D 02	1.98	0.07	0.1098171D 02
2.3	2.01	0.03	0.1231912D 02	1.98	0.06	0.1076846D 02
2.4	2.01	0.03	0.1167460D 02	1.98	0.06	0.1052643D 02
2.5	2.01	0.03	0.1111042D 02	1.98	0.05	0.1026209D 02
2.6	2.00	0.03	0.1061135D 02	1.99	0.04	0.9990196D 01
2.7	2.00	0.03	0.1016613D 02	1.99	0.04	0.9709568D 01
2.8	2.00	0.03	0.9765871D 01	1.99	0.04	0.9433672D 01
2.9	2.00	0.03	0.9403213D 01	1.99	0.03	0.9160931D 01
3.0	2.00	0.03	0.9072284D 01	1.99	0.03	0.8894538D 01
3.1	2.00	0.02	0.8766718D 01	2.00	0.03	0.8638420D 01
3.2	2.00	0.02	0.8483459D 01	2.00	0.03	0.8392691D 01
3.3	2.00	0.02	0.8220440D 01	2.00	0.02	0.8155587D 01
3.4	2.00	0.02	0.79751[illegible]D 01	2.00	0.02	0.7928061D 01
3.5	2.00	0.02	0.7745555D 01	2.00	0.02	0.7711422D 01
3.6	2.00	0.02	0.7529913D 01	2.00	0.02	0.7505225D 01
3.7	2.00	0.02	0.7326797D 01	2.00	0.02	0.7309974D 01
3.8	2.00	0.02	0.7134992D 01	2.00	0.02	0.7122148D 01
3.9	2.00	0.02	0.6953461D 01	2.00	0.02	0.6944221D 01
4.0	2.00	0.02	0.6781309D 01	2.00	0.02	0.6774672D 01
4.1	2.00	0.01	0.6617230D 01	2.00	0.01	0.6612864D 01
4.2	2.00	0.01	0.6460136D 01	2.00	0.01	0.6457016D 01
4.3	2.00	0.01	0.6310457D 01	2.00	0.01	0.6308229D 01
4.4	2.00	0.01	0.6167652D 01	2.00	0.01	0.6166065D 01
4.5	2.00	0.01	0.6031241D 01	2.00	0.01	0.6030111D 01
4.6	2.00	0.01	0.5900788D 01	2.00	0.01	0.5899985D 01
4.7	2.00	0.01	0.5775902D 01	2.00	0.01	0.5775331D 01
4.8	2.00	0.01	0.5656224D 01	2.00	0.01	0.5655820D 01
4.9	2.00	0.01	0.5541432D 01	2.00	0.01	0.5541145D 01
5.0	2.00	0.01	0.5431227D 01	2.00	0.01	0.5431024D 01
5.1	2.00	0.01	0.5325337D 01	2.00	0.01	0.5325193D 01
5.2	2.00	0.01	0.5223511D 01	2.00	0.01	0.5223409D 01
5.3	2.00	0.01	0.5125518D 01	2.00	0.01	0.5125446D 01
5.4	2.00	0.01	0.5031144D 01	2.00	0.01	0.5031094D 01
5.5	2.00	0.01	0.4940193D 01	2.00	0.01	0.4940157D 01
5.6	2.00	0.01	0.4852480D 01	2.00	0.01	0.4852455D 01
5.7	2.00	0.01	0.4767835D 01	2.00	0.01	0.4767817D 01
5.8	2.00	0.01	0.4686100D 01	2.00	0.01	0.4686087D 01
5.9	2.00	0.01	0.4607126D 01	2.00	0.01	0.4607118D 01
6.0	2.00	0.01	0.4530777D 01	2.00	0.01	0.4530771D 01
6.1	2.00	0.01	0.4456923D 01	2.00	0.01	0.4456919D 01
6.2	2.00	0.01	0.4385444D 01	2.00	0.01	0.4385441D 01
6.3	2.00	0.01	0.4316227D 01	2.00	0.01	0.4316225D 01
6.4	2.00	0.01	0.4249167D 01	2.00	0.01	0.4249165D 01
6.5	2.00	0.01	0.4184163D 01	2.00	0.01	0.4184162D 01
6.6	2.00	0.01	0.4121123D 01	2.00	0.01	0.4121123D 01
6.7	2.00	0.01	0.4059960D 01	2.00	0.01	0.4059960D 01
6.8	2.00	0.01	0.4000590D 01	2.00	0.01	0.4000590D 01
6.9	2.00	0.01	0.3942936D 01	2.00	0.01	0.3942936D 01
7.0	2.00	0.01	0.3886925D 01	2.00	0.01	0.3886925D 01
7.1	2.00	0.0	0.3832394D 01	2.00	0.0	0.3832394D 01

Table 2. e^2/R, V_+, V_- and $(V_+ - V_-)$ for various values of R.

(V_+, V_- and e^2/R are in e.v. and R is in units of $a_0 = 5.29 \times 10^{-11}$ meter)

R	e^2/R	V_+	V_-	$(V_+ - V_-)$
0.1	0.2721000D 03	0.9915382D 03	0.8400521D 03	0.1514861D 03
0.2	0.1360500D 03	0.4577075D 03	0.3192747D 03	0.1384328D 03
0.3	0.9070000D 02	0.2840353D 03	0.1617459D 03	0.1222893D 03
0.4	0.6802500D 02	0.1987872D 03	0.9275601D 02	0.1060312D 03
0.5	0.5442000D 02	0.1482373D 03	0.5743765D 02	0.9079961D 02
0.6	0.4535000D 02	0.1148298D 03	0.3780716D 02	0.7702259D 02
0.7	0.3887143D 02	0.9122249D 02	0.2639742D 02	0.6482507D 02
0.8	0.3401250D 02	0.7381676D 02	0.1962205D 02	0.5419471D 02
0.9	0.3023333D 02	0.6062741D 02	0.1559789D 02	0.4502952D 02
1.0	0.2721000D 02	0.5045272D 02	0.1325538D 02	0.3719734D 02
1.1	0.2473636D 02	0.4250392D 02	0.1195254D 02	0.3055138D 02
1.2	0.2267500D 02	0.3623637D 02	0.1130049D 02	0.2493588D 02
1.3	0.2093077D 02	0.3125602D 02	0.1103662D 02	0.2021940D 02
1.4	0.1943571D 02	0.2727334D 02	0.1099796D 02	0.1627537D 02
1.5	0.1814000D 02	0.2406450D 02	0.1107139D 02	0.1299311D 02
1.6	0.1700625D 02	0.2146301D 02	0.1118231D 02	0.1028070D 02
1.7	0.1600588D 02	0.1934363D 02	0.1128061D 02	0.8063023D 01
1.8	0.1511667D 02	0.1759662D 02	0.1133791D 02	0.6258710D 01
1.9	0.1432105D 02	0.1615172D 02	0.1133845D 02	0.4813267D 01
2.0	0.1360500D 02	0.1494454D 02	0.1127569D 02	0.3668845D 01
2.1	0.1295714D 02	0.1392800D 02	0.1115410D 02	0.2773895D 01
2.2	0.1236818D 02	0.1306258D 02	0.1098171D 02	0.2080870D 01
2.3	0.1183043D 02	0.1231912D 02	0.1076846D 02	0.1550666D 01
2.4	0.1133750D 02	0.1167460D 02	0.1052643D 02	0.1148168D 01
2.5	0.1088400D 02	0.1111042D 02	0.1026209D 02	0.8483295D 00
2.6	0.1046538D 02	0.1061135D 02	0.9990196D 01	0.6211542D 00
2.7	0.1007778D 02	0.1016613D 02	0.9709568D 01	0.4565641D 00
2.8	0.9717857D 01	0.9765871D 01	0.9433672D 01	0.3321993D 00
2.9	0.9382759D 01	0.9403213D 01	0.9160931D 01	0.2422817D 00
3.0	0.9070000D 01	0.9072284D 01	0.8894538D 01	0.1777460D 00
3.1	0.8777419D 01	0.8766718D 01	0.8638842D 01	0.1282971D 00
3.2	0.8503125D 01	0.8483459D 01	0.8392691D 01	0.9076732D-01
3.3	0.8245455D 01	0.8220440D 01	0.8155587D 01	0.6485270D-01
3.4	0.8002941D 01	0.7975160D 01	0.7928061D 01	0.4709866D-01
3.5	0.7774286D 01	0.7745555D 01	0.7711422D 01	0.3413337D-01
3.6	0.7558333D 01	0.7529913D 01	0.7505225D 01	0.2468819D-01
3.7	0.7354054D 01	0.7326797D 01	0.7308974D 01	0.1782304D-01
3.8	0.7160526D 01	0.7134992D 01	0.7122148D 01	0.1284402D-01
3.9	0.6976923D 01	0.6953461D 01	0.6944221D 01	0.9240225D-02
4.0	0.6802500D 01	0.6781309D 01	0.6774672D 01	0.6636875D-02
4.1	0.6636585D 01	0.6617230D 01	0.6612864D 01	0.4365658D-02
4.2	0.6478571D 01	0.6460136D 01	0.6457016D 01	0.3120269D-02
4.3	0.6327907D 01	0.6310457D 01	0.6308229D 01	0.2227281D-02
4.4	0.6184091D 01	0.6167652D 01	0.6166065D 01	0.1587625D-02
4.5	0.6046667D 01	0.6031241D 01	0.6030111D 01	0.1130243D-02
4.6	0.5915217D 01	0.5900788D 01	0.5899985D 01	0.8036536D-03
4.7	0.5789362D 01	0.5775902D 01	0.5775331D 01	0.5707698D-03
4.8	0.5668750D 01	0.5656224D 01	0.5655820D 01	0.4049188D-03
4.9	0.5553061D 01	0.5541432D 01	0.5541145D 01	0.2869517D-03
5.0	0.5442000D 01	0.5431227D 01	0.5431024D 01	0.2031427D-03
5.1	0.5335294D 01	0.5325337D 01	0.5325193D 01	0.1436686D-03
5.2	0.5232692D 01	0.5223511D 01	0.5223409D 01	0.1015094D-03
5.3	0.5133962D 01	0.5125518D 01	0.5125446D 01	0.7165557D-04
5.4	0.5038889D 01	0.5031144D 01	0.5031094D 01	0.5053667D-04
5.5	0.4947273D 01	0.4940193D 01	0.4940157D 01	0.3561145D-04
5.6	0.4858929D 01	0.4852480D 01	0.4852455D 01	0.2507332D-04
5.7	0.4773684D 01	0.4767835D 01	0.4767817D 01	0.1763945D-04
5.8	0.4691379D 01	0.4686100D 01	0.4686087D 01	0.1239997D-04
5.9	0.4611864D 01	0.4607126D 01	0.4607118D 01	0.8710231D-05
6.0	0.4535000D 01	0.4530777D 01	0.4530771D 01	0.6113956D-05
6.1	0.4460656D 01	0.4456923D 01	0.4456919D 01	0.4288530D-05
6.2	0.4388710D 01	0.4385444D 01	0.4385441D 01	0.3006058D-05
6.3	0.4319048D 01	0.4316227D 01	0.4316225D 01	0.2105708D-05
6.4	0.4251563D 01	0.4249167D 01	0.4249165D 01	0.1474073D-05
6.5	0.4186154D 01	0.4184163D 01	0.4184162D 01	0.1031261D-05
6.6	0.4122727D 01	0.4121123D 01	0.4121123D 01	0.7210314D-06
6.7	0.4061194D 01	0.4059960D 01	0.4059960D 01	0.5038293D-06
6.8	0.4001471D 01	0.4000590D 01	0.4000590D 01	0.3518549D-06
6.9	0.3943478D 01	0.3942936D 01	0.3942936D 01	0.2455847D-06
7.0	0.3887143D 01	0.3886925D 01	0.3886925D 01	0.1713181D-06
7.1	0.3832394D 01	0.3832394D 01	0.3832394D 01	0.1022968D-06

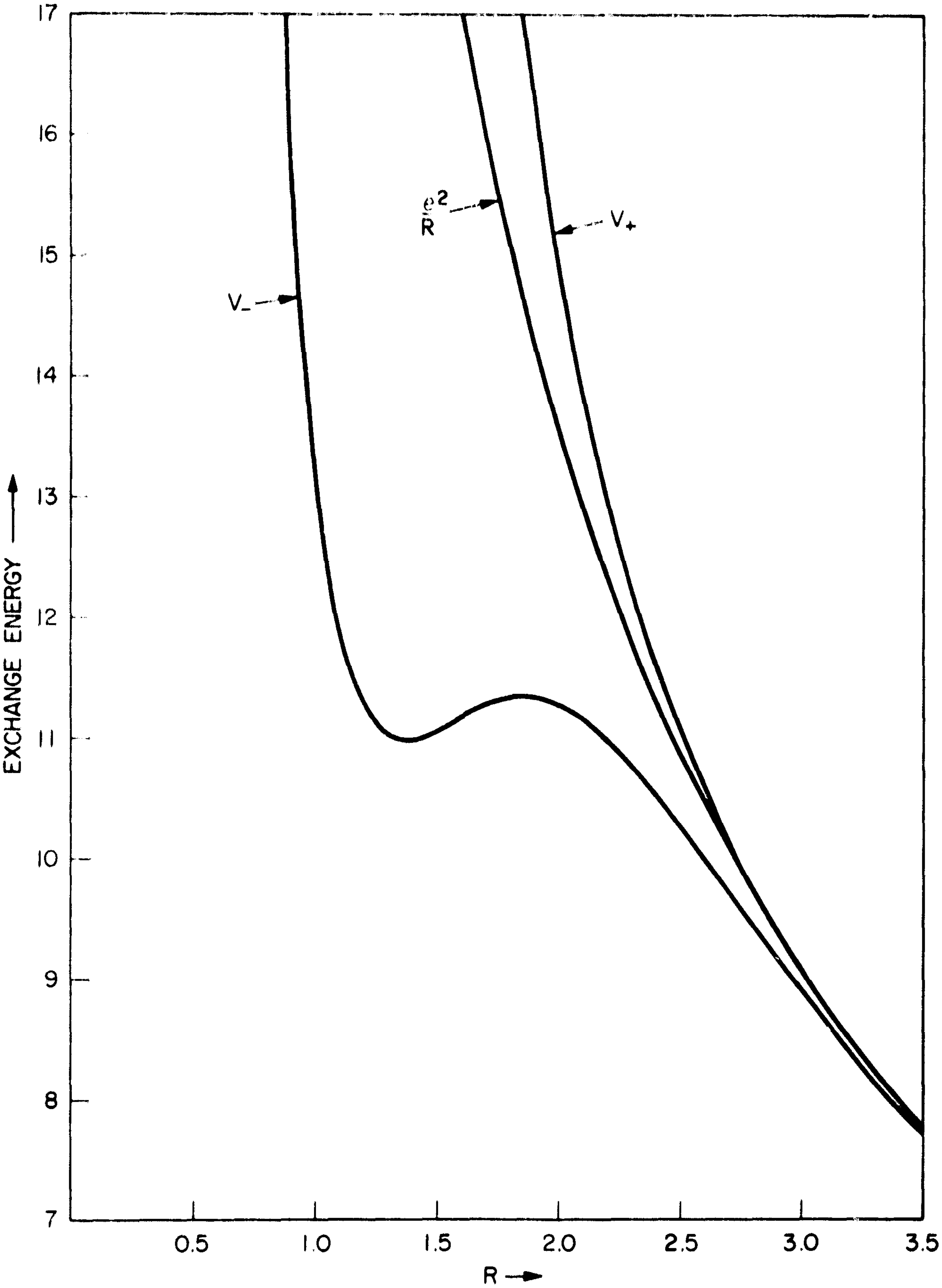

Figure 4. Plot of V+, V−, and e^2/R vs. internuclear distance. V_+, V_- and e^2/R are in e.v. and R is in units of $a_o = 5.29 \times 10^{-11}$ meter.

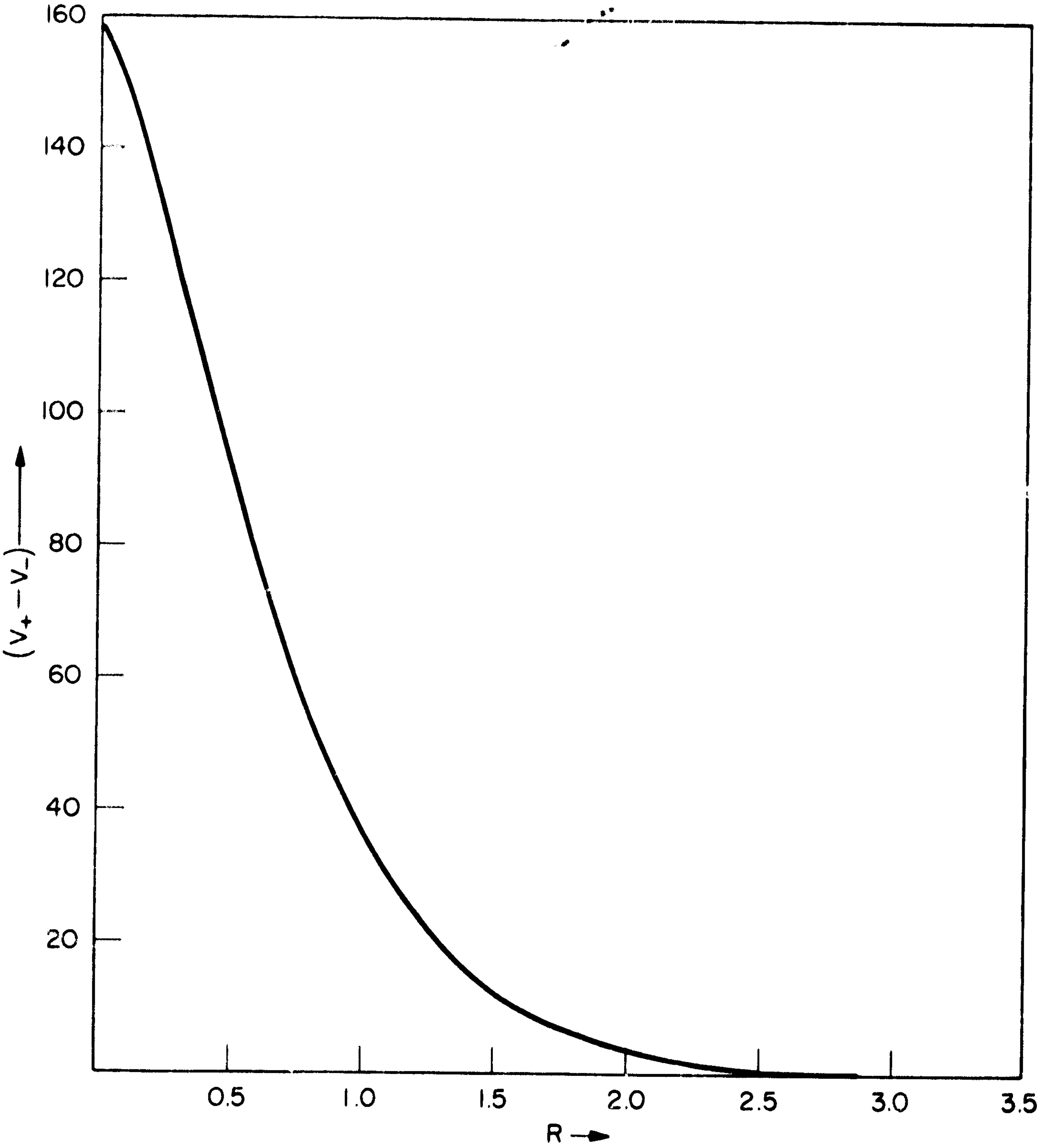

Figure 5. Plot of $(V_+ - V_-)$ vs. R. [$(V_+ - V_-)$ is in e.v. and R is in units of $a_0 = 5.29 \times 10^{-11}$ meter.]

RESULTS

The spin exchange cross section σ_{ex} for He$^+$ - He$^+$ was calculated for relative impact energies up to 1000 e.v. and is presented in Figure 6. It reaches a maximum value of 3.66 πa_0^2 at 85 e.v., and as can be seen from Table 3, falls rapidly to zero below 10 e.v.

Table 3. He$^+$ - He$^+$ spin exchange cross section for various values of impact energy.

E (e.v.)	σ_{ex} (πa_0^2)
5	9.95×10^{-8}
6	3.24×10^{-5}
7	1.81×10^{-3}
8	3.34×10^{-2}
9	2.65×10^{-1}
10	9.39×10^{-1}
20	2.77×10^{0}
40	3.48×10^{0}
60	3.63×10^{0}
80	3.65×10^{0}
85	3.66×10^{0}
100	3.65×10^{0}
200	3.53×10^{0}
400	3.31×10^{0}
600	3.16×10^{0}
800	3.06×10^{0}
1000	2.97×10^{0}

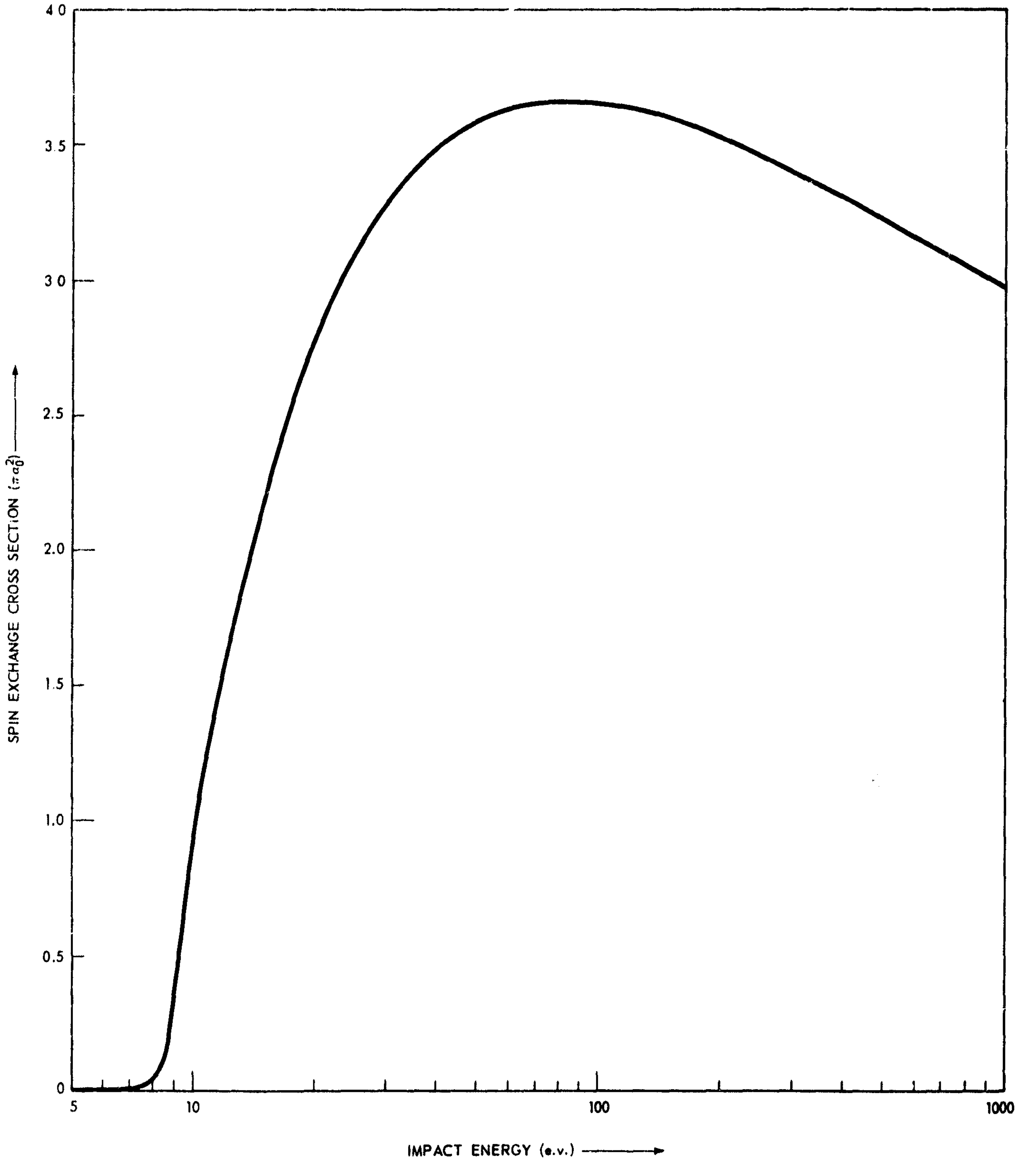

Figure 6. Plot of spin exchange cross section σ_{ex} vs. relative impact energy E.

At energies less than 5 e.v. the spin-spin interaction between the ions is the dominant force which leads to spin exchange. However, this interaction goes as β_0^2/R^3 (β_0 is the Bohr magneton) and the cross section will therefore continue to become smaller for decreasing values of energy.

CONCLUSIONS

The magnitude of the spin exchange between ions is essentially determined by the degree to which their outer electron wavefunctions overlap and hence, is dependent on their distance of closest approach, which for zero impact parameter b (see equation 20) is at its smallest value given by R_c(a.u.) = 27.21/E(e.v.). Now, the radius of the outer orbital of $(Hg^{199})^+$ is roughly four times greater then than that of He^+ and therefore, the spin exchange cross section between two He^+ ions with a given relative impact energy would essentially be equivalent to that of two $(Hg^{199})^+$ ions at one fourth this energy.[12] Using this criterion and the results given in Table 3, it can be seen that if the relative impact energy between the $(Hg^{199})^+$ ions confined in the quadrupole field of the proposed ionic frequency standard is choosen to be about 1.5 e.v., which should be easily achievable experimentally, then the spin exchange cross section for $(Hg^{199})^+$ - $(Hg^{199})^+$ will be negligible (about six orders of magnitude smaller than that due to H - H collisions in the hydrogen maser at typical operating temperatures) and hence, spin exchange between $(Hg^{199})^+$ ions can be ignored as a relaxation phenomenon.

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