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Classical many-body model for atomic collisions incorporating the Heisenberg and Pauli principles

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A novel, classical many-body model, previously introduced for nuclear collisions, has been extended to atomic and molecular structure, with the goal of providing a framework for atomic collisions. In addition to the usual kinetic and Coulomb potential terms, a momentum-dependent two-body potential acts between electron pairs of identical spin in order to approximate the Pauli constraint $r_{ij}p_{ij} \geq \hbar\xi p$, where ξ is a dimensionless parameter here set equal to 2.767. A similar potential is introduced to simulate the Heisenberg constraint, $r_{iN}p_{iN} = h$, where N refers to each nucleus. Because of these constraints, the atomic and molecular ground-state configurations are stable. The hydrogen ground state is given exactly. Calculations in H^-, He, Li, Ne, and Ar reproduce total ground-state energies to better than 15%; this is considerably better than the Thomas-Fermi model, in which the errors are approximately 28% for neon and 23% for argon. The resulting electrostatic potential is in general intermediate between Thomas-Fermi and Hartree-Fock calculations. $H_2{}^+$ and H_2 molecules are overbound; in contrast, the Thomas-Fermi model does not bind neutral molecules.

I. INTRODUCTION

Classical calculations for determining atomic collision cross sections have received a great deal of interest in the past 20 years because of their relative simplicity. Two approaches have been utilized; binary encounter theory and computer simulation of classical trajectories.

The binary encounter theory, pioneered by Thomas[1] and Williams[2] in 1928 and later repeated by Bryzinski,[3,4] Ochkur and Petrunkin,[5] and Stabler,[6] treats the electrons of an atom as essentially free particles during the time of the collision. The colliding particle may then be considered to undergo binary encounters with the individual electrons of the atom, all other electrons being ignored. The cross section for energy transfer (from particle 1 to particle 2) for two colliding charged particles was given by Williams as

$$\frac{d\sigma(\epsilon)}{dE}=\frac{\pi e^4 Z_1^2 Z_2^2 M_1}{M_2 E_1}\left(\frac{1}{\epsilon^2}+\frac{4}{3}\frac{E^2}{\epsilon^3}\right), \qquad (1)$$

where Z_1e is the charge on the incident particle, M_1 its mass, and E_1 its kinetic energy. Z_2e, M_2, and E_2 are the charge, mass, and kinetic energy of the second particle. This equation, or the more recent version of Vriens,[7] may then be integrated from the ionization energy of the electron to infinity and summed over all electrons in an atom to give the total ionization cross sections.

Equation (1) requires knowledge of the kinetic-energy distribution of the electrons. In normal calculations, this is obtained using information from experimental, Thomas-Fermi, or Hartree-Fock results. Details on the method may be found in the review articles of Bates and Kingston[8] or Burgess and Percival.[9]

Trajectory calculations by numerical integration have been used to solve three types of problems. Early calculations by Bunker,[10] Blais and Bunker,[11] Karplus and Raff,[12] and Herschbach[13] concentrated on molecular collisions. Individual atoms were treated as classical particles with semiempirical interparticle-force laws, and the equations of motion integrated to obtain molecular-reaction information.

Recently, attention has been given to the collisions of various charged particles, including electrons, protons, and ions of the form A^{q+}, with hydrogen atoms. Abrines and Percival[14] used three-body trajectories in analyzing the $H^+ + H$ collision by treating the protons and electron as classical particles with Coulombic interactions. Integration of the equations of motion gives ionization and charge-transfer cross sections. Other three-body trajectories by Banks *et al.*,[15] Olson *et al.*,[16-18] and Phaneuf *et al.*,[19] have extended the calculations to stripped ions and ions of the form A^{q+}. Four-body trajectories for $He^+ + H$ have been carried out by Becker and Mackellar.[20]

A third physical situation—the collision of a charged particle with an atom having a single highly excited electron—has been considered by Percival and Richards.[21] In this model, three-body-trajectory calculations (similar to those of a hydrogen atom) were made possible by treating the highly excited atom as an inert ion core with the single electron in a high-n classical Bohr orbit. Again, cross sections for ionization and charge transfer were determined by integration of the equations of motion.

In all of the above cases, the equations of motion are standard, and the integration is done numerically on a digital computer using one of several differential equation solving programs. Monte-Carlo initial conditions are used.

In the classical calculations given above, relatively simple approaches are taken either using approximations which ignore all but the simplest features of atomic structure or considering only one-electron atoms and ions where atomic structure is classically allowed. This is perhaps because the only atomic models which have been able to give good agreement with experimental ground-state atomic structure are the quantum-mechanical Hartree-Fock model and the semiclassical Thomas-Fermi model, neither of which is suitable for classical collisional calculations. Furthermore, a truly classical atom with unconstrained electrons is unstable and collapses, emitting electrons.

What is needed then is a simplified theory of atomic structure which, while retaining essential ground-state features, remains useful for collision calculations. Such a model is introduced in this paper by simulating the Heisenberg uncertainty principle and Pauli exclusion principle with constraints of the form $r_i p_i \geq \xi_H \hbar$ for all electrons and $r_{ij} p_{ij} \geq \xi_p \hbar$ for identical electron pairs. The constraints are approximated by potentials of the form

$$V_c(p,r) = r^{-2} f(rp) . \tag{2}$$

The particular form chosen is

$$V_c = \frac{(\xi\hbar)^2}{4\alpha r^2 m} \exp\left\{\alpha\left[1-\left(\frac{rp}{\xi\hbar}\right)^4\right]\right\} . \tag{3}$$

The equations of motion are determined from the Hamiltonian and solved analyticically, in simple cases, or numerically, in more complex cases, to yield the ground-state configurations of atoms. We believe this classical model will be of use in a wide variety of collisional calculations.

II. HEISENBERG AND PAULI CONSTRAINTS

In an earlier paper Wilets, Henley, Kraft, and Mackellar[22] proposed a classical model for nuclear collisions where the Pauli exclusion principle is simulated by a momentum-dependent two-body potential. The model proposed below is extended to include the Heisenberg uncertainty principle as well. This is accomplished by requiring that the magnitudes and position of each electron relative to the nucleus obey the relation $r_i p_i \geq \xi_H$, where $\vec{r}_i$ is the position of the ith electron, $\vec{p}_i$ is the momentum of the ith electron, and ξ_H is a dimensionless constant which must be determined. (Here, as in the remainder of the paper, we utilize atomic units $\hbar = m_e = e = 1$.) It is the Heisenberg principle which prevents atomic collapse.

The Pauli principle requires that two identical fermions have orthogonal wave functions. Classically this means that any two electrons having the same spins cannot occupy the same volume of phase space. We effect this by requiring that $r_{ij} p_{ij} \geq \xi_p$, where $\vec{r}_{ij}$ is the relative position and $\vec{p}_{ij}$ is the relative momentum of the ith and jth identical electrons, and ξ_p is another dimensionless constant which must be determined. No constraint is placed on the relative positions and momenta of electrons with opposite spins.

Once the constants ξ_H and ξ_p have been determined, these constraints, together with the classical Hamiltonian

$$H = \sum_i \left(\frac{p_i^2}{2} - \frac{Z}{r_i}\right) + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} , \tag{4}$$

give a complete description of the model and may be used to determine the ground-state configurations of atoms.

The constant ξ_H is obtained by applying the model to the hydrogen atom. It is clear that in the ground, or lowest-energy, configuration the condition $rp = \xi_H$ rather than $rp > \xi_H$ must hold. The Hamiltonian is

$$H = p^2/2 - 1/r . \tag{5}$$

Using the constraint we have

$$H = \xi_H^2/2r^2 - 1/r , \tag{6}$$

or for the stationary state

$$\frac{\partial H}{\partial r} = \frac{-\xi_H^2}{r^3} + \frac{1}{r^2} = 0 , \tag{7}$$

and hence $r = \xi_H^2, p = 1/\xi_H$, and $E = -1/2\xi_H$. From this condition we find $\xi_H = 1$.

Obtaining the value for ξ_p is somewhat more difficult, and as yet no final answer has been found. Two approximations are employed to calculate the energy of an infinite system of noninteracting fermions; the parameter ξ_p is then adjusted to reproduce the Fermi gas energy. In both cases, the electrons are assumed to be in a close-packed, face-centered-cubic array. One cell is shown in Fig. 1. The determination of the $\vec{p}_i$ that produce the lowest energy is an interesting problem in lattice theory.

The first method, used in Ref. 22, assumes that $\langle \vec{p}_i \cdot \vec{p}_j \rangle = 0$ in the array, and that all p_i are the same. In this paper, we retain the assumption that all p_i are the same; however, we assume that particles separated by a distance greater than the nearest-neighbor distance do not appreciably affect each other. We then need only consider the four particles which are mutual nearest neighbors, each separated from the others by a distance a (see Fig. 1). The constraint equa-

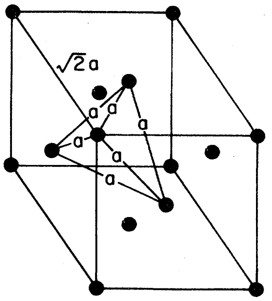

FIG. 1. One cell of a face-centered-cubic array showing four mutual nearest neighbors.

tion reduces to a $p_{ij} = \xi_p$, where i and j run over the four particles.

Since the momenta of the four particles differ only in angle, the angles between the momenta must be equal, and hence the momenta must point to the four corners of a regular tetrahedron. The equation of constraint becomes

$$ap_{ij} = \tfrac{1}{2}[a(p^2 + p^2 - 2p^2 \cos\theta)^{1/2}]$$
$$= \tfrac{1}{2}ap(\tfrac{8}{3})^{1/2} = (\tfrac{2}{3})^{1/2} ap = \xi_p \,, \tag{8}$$

where the tetrahedral angle given by $\cos\theta = -\frac{1}{3}$ has been substituted. The energy is

$$E = \tfrac{1}{2}p^2 = \tfrac{3}{4}\xi_p^2/a^2 \,, \tag{9}$$

with volume per particle

$$v = \tfrac{1}{4}(\sqrt{2}a)^3 = n^{-1} \,. \tag{10}$$

The Fermi energy is well known to be

$$E = \tfrac{3}{10}\pi^2\left(\frac{6}{\pi}n\right)^{2/3} . \tag{11}$$

Equating this to the classical result we have

$$\tfrac{3}{10}\pi^2\left(\frac{6}{\pi}\frac{4}{(\sqrt{2}a)^3}\right)^{2/3} = \frac{3}{4}\frac{\xi_p^2}{a^2} \tag{12}$$

or

$$\xi_p = [\tfrac{4}{5}\pi^2(3/\pi)^{2/3}]^{1/2} = 2.767 \,. \tag{13}$$

The value calculated by the previous method is 2.14.

It should be emphasized that both of the values are based on the assumptions that (i) the particles form a crystalline face-centered-cubic structure, and (ii) the magnitudes of the momenta of all particles are the same. An alternate approach would be to fit the parameter ξ_p to finite systems (e.g., atoms). We are currently engaged in further research to determine a more suitable value.

III. APPLICATION TO SIMPLE ATOMS AND MOLECULES

A. Two-electron atoms and ions

It is possible to make analytic calculations, using the constraint conditions, for one-, two-, and three-electron systems. For the two-electron case the electrons lie in a plane with the nucleus. By symmetry, we expect they will lie in a straight line. Since the electrons are not identical, no Pauli constraint is required. The Hamiltonian is

$$H = p_1^2/2 + p_2^2/2 - Z/r_1 - Z/r_2 + 1/r_{12} \,, \tag{14}$$

with constraints

$$p_i r_i \geqslant \xi_H \,,$$

and where

$$r_{12} = |\vec{r}_1 - \vec{r}_2| = (r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta)^{1/2}.$$

Minimization with respect to p_1 and p_2 is obtained when the Heisenberg constraint is taken to be an equality. Minimization with respect to r_1 and r_2 yields

$$r_1 = r_2 = 4\xi_H^2/(4Z-1) \,,$$
$$p_1 = p_2 = (4Z-1)/4\xi_H, \quad E = -(4Z-1)^2/16\xi_H^2 \,. \tag{15}$$

For the helium atom with $Z = 2$ and $\xi_H = 1$ (as calculated earlier), we find

$$r = \tfrac{4}{7}, \quad p = \tfrac{7}{4}, \quad E = \tfrac{49}{16} = -3.0625 \,. \tag{16}$$

This is to be compared with the experimental value[23] for E of -2.862.

Since Thomas-Fermi theory does not bind negative ions, it is of some interest to consider the H^- ion, a two-electron ion with $Z = 1$. The solution is

$$r = \tfrac{4}{3}, \quad p = \tfrac{3}{4}, \quad E = -\tfrac{9}{16} = -0.5625 \,, \tag{17}$$

which indicates that the ion is bound by $-\frac{1}{16}$ relative to H. The experimental value[24] is -0.0277. The fact that it binds at all is encouraging, even though it does overbind.

B. Three-electron atoms and ions

The three-electron case has general constraints

$$r_i p_i \geqslant \xi_H \quad \text{and} \quad r_{13}p_{13} \geqslant \xi_p \,,$$

and the Hamiltonian is

$$\sum_{i=1}^{3}\left(\frac{p_i^2}{2} - \frac{Z}{r_i}\right) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} . \tag{18}$$

The three electrons and the nucleus are again expected to be coplanar since any configuration of the electrons removing the nucleus from the same plane will cause an increase in energy. The positions may be described as in Fig. 2. To obtain an

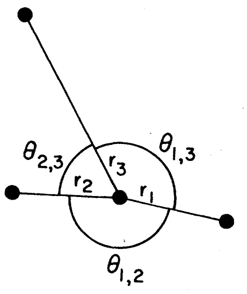

FIG. 2. Geometry of the three-electron case.

approximate solution for the ground-state configuration, we assume the third electron is somewhat further from the nucleus than the other two electrons. The equations may then be simplified by treating the third electron as a perturbation on the two-electron system and ignoring terms of order r_1/r_3 and $\Delta\theta$. The simplifications give

$$
\begin{aligned}
&r_1 \cong r_2 \cong r, \quad p_1 \cong p_2 \cong p, \quad \theta_{12} \cong \pi, \\
&r_{12} = (r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12})^{1/2} \cong 2r\,, \\
&r_{13} = (r_1^2 + r_3^2 - 2r_1 r_3 \cos\theta_{13})^{1/2} \cong r_3\,, \\
&r_{23} = (r_2^2 + r_3^2 - 2r_2 r_3 \cos\theta_{23})^{1/2} \cong r_3\,, \\
&p_{13} = (p_1 + p_3) \cong p\,,
\end{aligned}
\tag{19}
$$

and the Hamiltonian reduces to

$$
H = p^2 + p_3^2/2 - (Z - \tfrac{1}{2})/r - (Z-2)/r_3 \tag{20}
$$

with constraints

$$
rp = \xi_H, \quad r_3 p_3 = \xi_H, \quad r_3 p/2 = \xi_p\,.
$$

This is particularly simple to solve for the ground configuration giving

$$
\begin{aligned}
r &= \frac{2(\xi_H^2 + \xi_H^4/8\xi_p^2)}{2Z - \frac{1}{2} + (Z-2)\xi_H/2\xi_H}\,, \\
r_3 &= (4\xi_p/\xi_H)\frac{\xi_H^2 + \xi_H^4/8\xi_p^2}{2Z - \frac{1}{2} + (Z-2)\xi_H/\xi_p}\,, \\
p &= \frac{\xi_H[2Z - \frac{1}{2} + (Z-2)\xi_H/2\xi_p]}{2(\xi_H^2 + \xi_H^4/8\xi_p^2)}\,, \\
p_3 &= (\xi_H^2/4\xi_p)\,\frac{2Z - \frac{1}{2} + (Z-2)\xi_H/2\xi_p}{\xi_H^2 + \xi_H^4/8\xi_p^2}\,, \\
E &= \frac{[2Z - \frac{1}{2} + (Z-2)\xi_H/2\xi_p]^2}{4\xi_H^2 + \xi_H^4/8\xi_p^2}\,.
\end{aligned}
\tag{21}
$$

We may apply this result to the lithium ion with $Z = 3$ to obtain

$$
\begin{aligned}
&r = 0.368, \quad r_3 = 2.036\,, \\
&p = 2.717, \quad p_3 = 0.491, \quad E = -7.938\,.
\end{aligned}
\tag{22}
$$

Again, this may be compared with the experimental binding energy[23] of -7.369.

C. Molecules

Utilizing the method for molecules is only slightly more difficult in principle than for atoms. We add the necessary terms to the Hamiltonian and insure that $r_{iN} p_i \geqslant \xi_H$ for all nuclei N. $\vec{r}_{iN}$ is the distance between the ith electron and the Nth nucleus. The equations become

$$
H = \sum_i p_i^2 + \tfrac{1}{2}\sum_{n \neq m} \frac{z_n z_m}{r_{nm}} - \sum_{i,n} \frac{z_n}{r_{in}} + \tfrac{1}{2}\sum_{i \neq j} \frac{1}{r_{ij}}\,, \tag{23}
$$

subject to the constraints $r_{iN} p_i \geqslant \xi_H$ and $r_{ij} p_{ij} \geqslant \xi_p$.

The ground state of the simplest neutral molecule, H_2, may be determined by appealing to symmetry to reduce the complexity of the Hamiltonian. The molecular configuration should be as shown in Fig. 3. It is sufficiently general to restrict consideration to $r\cos\theta \leqslant a$. We may divide the problem into two regions, $r\cos\theta < a$ and $r\cos\theta = a$.

In the region $r\cos\theta < a$ the Hamiltonain is

$$
H = \frac{1}{2a} - \frac{2}{r} + \frac{1}{2(r^2 + a^2 - 2ra\cos\theta)^{1/2}} - \frac{2}{(r^2 + 4a^2 - 4ar\cos\theta)^{1/2}} + p^2\,, \tag{24}
$$

with constraint $rp = 1$. Requiring $\partial H/\partial\theta = 0$, we find $\cos\theta = \frac{3}{4} r/a$, which gives

$$
\frac{\partial H}{\partial r} = \frac{2}{r^2} - \frac{2r^2}{(4a^2 - 2r^2)^{3/2}} - \frac{2}{r^3} = 0 \tag{25}
$$

for the stationary state.

On the axis where $r\cos\theta = a$, the Hamiltonian reduces to

$$
H = \frac{1}{2a} - \frac{4}{r} + \frac{1}{2(r^2 - a^2)^{1/2}} + p^2\,, \tag{26}
$$

again with constraint $rp = 1$. The stationary condition is

$$
4/r^2 - r/2(r^2 - a^2)^{3/2} - 2/r^3 = 0\,. \tag{27}
$$

The equations may be solved numerically as a function of a to give the minimum energy. In Fig. 4, we plot the absolute minimum energy, $\min(E_{r\cos\theta = a}, E_{r\cos\theta < a})$ (solid line), together with the semiempirical energy (dashed line), as a func-

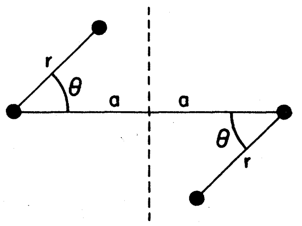

FIG. 3. Geometry of H_2.

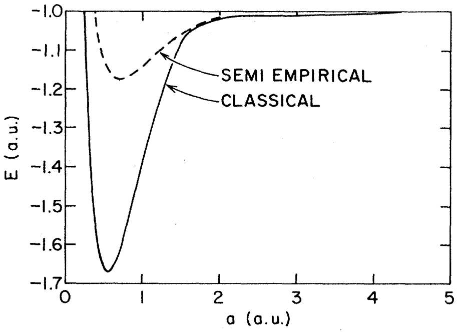

FIG. 4. Potential as a function of atom separation for H_2.

tion of a. The minimum energy is -1.672 at $a=0.55$ and $r=0.776$ with the electrons on the axis. The binding energy is considerably deeper than the experimental value[25] of -2.174, which lies at $a=0.742$.

It is also of interest to consider the H_2^+ ion. This is done with exactly the same approach as that used for H_2. In Fig. 5 we plot the minimum configuration energy as a function of internucleus separation. The lowest energy is $-\frac{9}{8}$ with $a=\frac{4}{3}$ and the electron centered between the two nuclei. Again this result is substantially overbound compared with the experimental value[25] of -0.597 at $a=1.00$.

IV. NUMERICAL MODEL

Using the above model to calculate the ground states of atoms becomes increasingly more difficult for higher atomic numbers. To obtain solutions for these atoms, numerical-integration methods are employed by replacing the constraints $r_i p_i \geq \xi_H$ and $r_{ij} p_{ij} \geq \xi_p$ with potentials. One family of such potentials has been given in Ref. 22 as $V_c(p,r)=r^{-2}f(pr)$, and the particular form used is

$$V_c(p,r)=(\xi^2/4\pi r^2)\exp\{\alpha[1-(rp/\xi)^4]\}\,, \tag{28}$$

where r, p, and ξ may be either r_i, p_i, and ξ_H or r_{ij}, p_{ij}, and ξ_p. The hardness parameter α is adjustable, a large value giving nearly the constraints $rp \geq \xi$, and a small value giving weak constraints. In this paper we use $\alpha=5$. This form identifies V_c with the kinetic-energy term as will be seen below by the virial theorem.

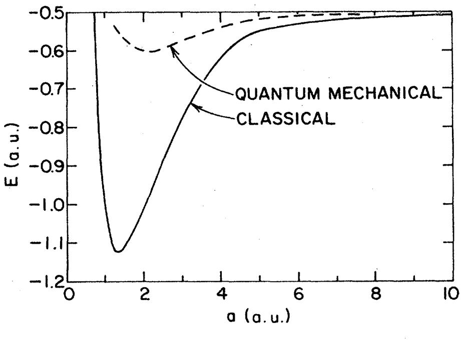

FIG. 5. Potential as a function of atom separation for H_2^+.

Using this potential the classical Hamiltonian may be written as

$$H=\sum_i[\tfrac{1}{2}p_i^2-Z/r_i+V_H(p_i,r_i)] + \tfrac{1}{2}\sum_{i\neq j}[1/r_{ij}+\delta_{s_i s_j}V_p(p_{ij},r_{ij})]\,. \tag{29}$$

Here $\delta_{s_i s_j}$ is 1 if the spins of the ith and jth electrons are the same and 0 if they are different. Note that it is possible to violate the constraint if the soft potential is used.

Some interesting results may be obtained analytically without actually solving the Hamiltonian. First, the Heisenberg and Pauli potentials combine with the kinetic energy to satisfy a modified virial theorem. We introduce a scale parameter by replacing p with p/λ and r with λr. The Hamiltonian becomes

$$H(\lambda)=\sum_i\left(\frac{p_i^2}{2\lambda^2}-\frac{Z}{\lambda r_i}+\frac{1}{\lambda^2 r_i^2}f(r_i p_i)\right) + \sum_{i\neq j}\left(\frac{1}{\lambda r_{ij}}+\delta_{s_i s_j}\frac{1}{\lambda^2 r_{ij}^2}f(r_{ij}p_{ij})\right)\,. \tag{30}$$

If p_i and r_i are the solutions which minimize the original Hamiltonian, then $H(\lambda)$ is minimized at $\lambda=1$. This gives

$$-E_p=2(E_k+V_H+V_p)\,, \tag{31}$$

which is our modified virial theorem.

Since we have not determined definite values for ξ_p and ξ_H, it is interesting to consider the effect scaling them has on the Hamiltonian. We let $\xi\rightarrow\lambda\xi$, $r\rightarrow\lambda^2 r$, and $p\rightarrow p/\lambda$, which satisfies the requirement $rp/\xi\rightarrow rp/\xi$. Then

$$H(\lambda)=\sum_i\left[\frac{p_i^2}{2\lambda^2}-\frac{Z}{\lambda^2 r_i}+\frac{\xi_H^2}{\lambda^2 r_i^2}g\left(\frac{r_i p_i}{\xi_H}\right)\right] + \tfrac{1}{2}\sum_{i\neq j}\left[\frac{1}{\lambda^2 r_{ij}}+\delta_{s_i s_j}\frac{\xi_p^2}{\lambda^2 r_{ij}^2}g\left(\frac{r_{ij}p_{ij}}{\xi_p}\right)\right]=\frac{1}{\lambda^2}H\,. \tag{32}$$

The Hamiltonian scales by $1/\lambda^2$.

The substitution of the soft potentials for the hard constraints leads to a change in the energy, position, and momentum of the ground configuration. This may be seen by considering the case of the hydrogen atom. The Hamiltonian is

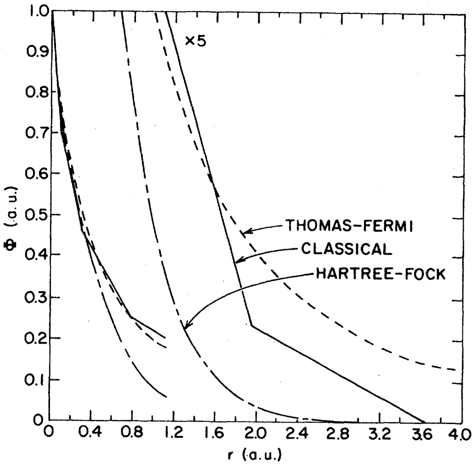

FIG. 6. Dimensionless potential function Φ as a function of radial distance from the nucleus for neon.

$$H = \frac{p^2}{2} - \frac{1}{r} + \frac{\xi_H^2}{4\alpha r^2} \exp\left\{\alpha\left[1 - \left(\frac{pr}{\xi_H}\right)^4\right]\right\}. \tag{33}$$

In the ground or stationary configuration, $\partial H/\partial p = 0$ by construction, and we require $\partial H/\partial r = 0$. This gives

$$\begin{aligned} r &= \xi_H^2(1 + 1/2\alpha), \\ p &= 1/\xi_H(1 + 1/2\alpha), \\ E &= (1/2\xi_H^2)1/(1 + 1/2\alpha). \end{aligned} \tag{34}$$

By making the renormalization $\xi \to \xi/(1 + \frac{1}{2}\alpha)^{1/2}$ as above, we may obtain the correct r and E for the hydrogen atom.

Although it is not obviously the best approach, we have made such a correction in our numerical model. If solutions to the constraint problem are desired, it is perhaps better to allow α to become large enough that the correction is negligible.

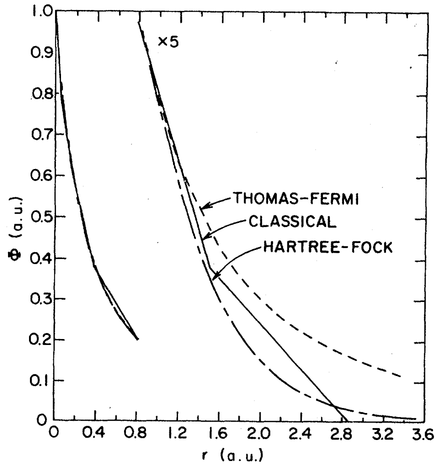

FIG. 7. Dimensionless potential function Φ as a function of radial distance from the nucleus for argon.

TABLE I. Some moments for neon.

	Classical	HF (Ref. 22)
$\langle 1/r\rangle$	3.352	3.111
$\langle r\rangle$	1.177	0.789
$\langle r^2\rangle^{1/2}$	1.614	0.968
$\langle p\rangle$	3.495	
$\langle p^2\rangle$	5.167	5.070

V. NUMERICAL CALCULATIONS OF THE GROUND CONFIGURATIONS

We have obtained a numerical value for the ground configuration in one of two ways. Originally, we used a numerical integration method similar to that given in Ref. 22. More recently, we utilized an International Mathematical and Statistical Libraries subroutine for minimizing multivariable functions[26] which gives substantial savings over the previous method. This method is also easier to use, requiring only a subroutine to evaluate the energy and a set of initial conditions.

For initial conditions, we set the electrons on a regular grid in the first quadrant (the nucleus being at the origin) and arbitrarily set the momentum $\vec{p}$ equal to the position $\vec{r}$. The routine was able to converge to the ground state although it did prove advantageous to move electrons which strayed far from the center back in. These initial conditions are very poor, and any improvement would undoubtedly give significant saving in the time required for convergence.

We have applied the model to helium, lithium, neon, and argon, obtaining ground-state energies of -3.062, -8.015, -145.5, and -566.0. The value for helium is a test of the numerical model (the analytic value is 3.060). The value for lithium tests both the numerical method and the perturba-

TABLE II. Some moments for argon.

	Classical	HF (Ref. 22)
$\langle 1/r\rangle$	4.032	3.873
$\langle r\rangle$	1.007	0.893
$\langle r^2\rangle^{1/2}$	1.369	1.203
$\langle p\rangle$	5.014	
$\langle p^2\rangle^{1/2}$	7.602	7.258

TABLE III. Contributions to the total energy for neon.

E_p	E_k	v_H	v_p	Total
−291.1	133.5	8.9	3.1	−145.5

tion method (−7.938). The values for neon and argon may be compared with the Hartree-Fock[27] values −128.5 and −526.8, and the Thomas-Fermi[23] values −165.6 and −652.7.

Since the purpose of the model is to approximate atomic structure for use in classical collisions, some comparison of the structure with the quantum-mechanical Hartree-Fock and Thomas-Fermi models is advisable. A quick comparison is given by the total-energy figures above. This, however, being strongly dominated by the inner electrons, is inadequate for any serious consideration, and a more careful comparison of electron positions must be made. The straightforward approach of comparing electron densities has been discarded because of the ambiguities in assigning densities to point electrons. Instead, the Hartree-Fock and Thomas-Fermi potentials are compared with the monopole component of the electrostatic potential, which is given in the model by

$$V_0=\sum_i \frac{1}{r_>}-\frac{Z}{r}, \tag{35}$$

where

$$r_> = \max(r, r_i). \tag{36}$$

The comparison is enhanced by considering the dimensionless potential function

$$\Phi = -(r/Z)V_0. \tag{37}$$

Finally, we compare some of the moments of the electron-density functions. Such comparisons are made here for neon and argon.

The dimensionless potential function Φ is given as a function of r for the classical model (solid line), Thomas-Fermi model (dashed line),[28] and Hartree-Fock model (long and short dash)[29,30] in Fig. 6 for neon and Fig. 7 for argon. The moments $\langle 1/r\rangle$, $\langle r\rangle$, and $\langle r^2\rangle^{1/2}$ are compared with Hartree-Fock values in Tables I and II, and, as a matter of interest, the moments $\langle p\rangle$ and $\langle p^2\rangle$ are also given. Note that both atoms have the same general features: The dimensionless electrostatic potential at first lies below both TF and HF curves; in the middle it is above the TF curve, and finally it falls to zero between the two curves. In both cases, the values of $\langle r\rangle$ and $\langle r^2\rangle^{1/2}$ are too large, indicating that the outer electrons extend too far out (this is not too surprising since both Ne and Ar are closed-shell atoms and especially compact). The value of $\langle 1/r\rangle$ is also too large, indicating that the inner electrons are too close. One could attempt to improve these values by varying α, ξ_H, and ξ_p. Tables III and IV give the potential energy, kinetic energy, Heisenberg and Pauli energies, and the total energy. Figure 8 gives the logarithm of the radial positions of the electrons. Table V summarizes the energies for the atoms we have completed.

TABLE IV. Contributions to the total energy for argon.

E_p	E_k	v_H	v_p	Total
−1132	520.2	28.4	17.4	−566.0

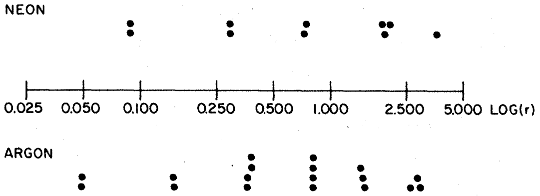

FIG. 8. Radial positions of the electrons for neon and argon plotted on a logarithmic scale.

VI. CONCLUSIONS

We have presented here a classical atomic model which incorporates features of the Heisenberg and Pauli principles. The main purpose of the model is to provide a framework for many-body atomic-collision calculations.

The ground-configuration energies of helium, lithium, neon, and argon given in the model are within 15% of the experimental or Hartree-Fock values. The negative ion, H^-, is bound with an energy relative to H of −0.0625. The H_2^+ and H_2 molecules, in contrast to the Thomas-Fermi result, which does not bind neutral molecules, are

TABLE V. Summary of the (−) energies of completed systems.

System	Classical	TF	HF	Experimental
H^-	0.5625			0.5277
He	3.0625	3.8740	2.8359	2.8900
Li	7.938	9.978	7.432	7.44
Ne	145.5	165.6	128.5	
Ar	566.0	652.7	526.8	

overbound. We do not expect the model to give molecular structure well since molecular binding is a very sensitive function of outer-shell structure.

Extensions of the model would include: (a) The determination of an optimal set of parameters α, ξ_H, and ξ_p; (b) The search for another form for the Heisenberg and Pauli potentials; and (c) The identification of a better approach to the Heisenberg uncertainty principle, in the case of multicenter problems (e.g., molecules).

Applications of the mode include: (i) Electron-atom scattering, (ii) atom-atom and ion-ion scattering, (iii) muon scattering and capture, and (iv) molecular scattering. Collision calculations are capable of yielding full "microscopic" information, such as energy loss, differential scattering cross sections, ionization, electron transfer, and, in the case of muons, the characteristics of the capture orbits. Calculations are in progress on several of these problems, and results will be presented in a forthcoming paper.

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