Quasiclassical effective Hamiltonian structure of atoms with $Z = 1$ to 38

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The Kirschbaum-Wilets quasiclassical, many-body atomic model [Phys. Rev. A **21**, 834 (1980)] is applied to atoms and ions having $1 \leq Z \leq 38$. An efficient method was found to search for the global minimum of the energy functional. A quasiclassical shell structure is shown to result from the Hamiltonian formulation in terms of momentum-dependent potentials representing quantum-mechanical effects codified in the Heisenberg and Pauli principles. Along with ionization and correlation energies, the ground-state configurations are presented for use as initial conditions in various dynamical calculations.

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I. INTRODUCTION

The classical-trajectory Monte Carlo (CTMC) method was invented in the early 1960s [1] to put new digital computers to work calculating cross sections for atom-molecule collisions; in this method, individual atoms are treated as classical particles moving on a quantum-mechanical potential-energy surface. A bold next step was taken by Abrines and Percival [2], who applied the CTMC method to the electronic motion as well as the nuclear motions in p+H collisions. The method was justified by the correspondence principle for collisions with Rydberg-atom targets, but it was evident that the results were surprisingly good even for collisions with the ground state. Since its first application, the CTMC method has been much used in the calculation of ionization and electron-capture cross sections for ion-atom collisions at intermediate velocities ($v \sim 1$ a.u.) [3]; it has also had considerable success for collisions of negatively charged particles ($\mu^-, \bar{p}$), even at very low velocities, and exotic atom formation [4].

The allure is that a classical Hamiltonian system is easily integrated on a computer with no problems presented by the electronic continuum, choice of coordinates or basis set, etc. Generally these calculations have been limited to one-particle transitions because of the unsuitability of classical dynamics for the pure Coulomb dynamics of multielectron systems. Though there exist interesting special orbits of (at least) two-electron atoms that are classically stable [5], in general the classical atom is unstable with respect to autoionization due to the absence of the lower bounds on the electron energies imposed by quantum mechanics. In any event, such special orbits may be expected to destabilize when altered by nonperturbative external forces. Even in single-electron systems such as $He^+ + H^+$, there is a problem associated with the tendency of a classically transferred electron to go into an orbital of H having unphysically large binding energy [6]. Nonetheless, the CTMC technique has been of great practical computational importance. Thus a generalization improving the shortcomings and allowing direct application to multielectron systems would be highly desirable. Of course, the goal is a practical tool, not a fundamental theory, which is already provided by quantum mechanics.

The formulation of such a model was suggested by Wilets *et al.* over a decade ago for application to heavy-ion (nuclear) collisions [7] and later to atomic collisions [8]. Proceeding heuristically, they introduced momentum-dependent effective two-body potentials to enforce the quantal effects reflected in atomic structure by the Heisenberg uncertainty and Pauli exclusion principles. Only two fundamental parameters, one associated with each principle, have to be fixed by resorting to quantum mechanics. Kirschbaum and Wilets [8] determined the former by matching the energy of the ground-state hydrogen atom and the latter by matching the Fermi energy of an infinite electron gas. It turns out that this simple formulation suffices to stabilize all atoms. Perhaps more surprising, the model yields atomic energies amazingly close to their accurate energies and a shell structure — though it will be shown that the shell structure does not fully correspond to that of real atoms.

Most applications of the Kirschbaum-Wilets quasiclassical method, which has come to be known as Fermi molecular dynamics (FMD), have been made to two-electron systems (there are a few calculations on systems with more electrons). These applications have been to scattering [6,9] as well as to atoms in intense fields [10,11]. In the latter problem, experiments suggest that correlation sometimes plays an important role in the times and energies of ionization [12]. Such correlation is difficult to take into account in quantum-mechanical calculations, but simply treated by FMD.

A systematic treatment of collisions by FMD has not yet been attempted. In fact, it would seem that a thorough examination of the quasiclassical structure of the isolated atoms would be in order first. That examination

is the objective of the present work. In its own right, the investigation of quasiclassical atomic structure is of interest for the insight it may lend to real atomic behavior (especially electron correlation) and as a preliminary for semiclassical treatments with topological quantization.

II. FORMULATION

A. Quasiclassical model

The quasiclassical Hamiltonian proposed by Kirschbaum and Wilets (KW) [8] for atoms consists of the usual kinetic energy and Coulomb terms subject to constraints representing the quantal effects of electron waves and symmetry. These effects are manifested in the Heisenberg and Pauli principles and can be realized by the constraints [13] $r_i p_i \geq \xi_H \hbar$ and $r_{ij} p_{ij} \geq \xi_P \hbar$, respectively, where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and momentum of the ith electron with respect to the nucleus and $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{p}_{ij} = \frac{1}{2}(\mathbf{p}_j - \mathbf{p}_i)$. [Note: The factor $\frac{1}{2}$ in the latter comes from the fact that $\mathbf{p}_{ij}$ is in the electron-electron c.m. system, while $\mathbf{p}_i$ and $\mathbf{p}_j$ are with respect to the (heavy) nucleus.] The two parameters ξ_H and ξ_P, of order unity, can be determined by comparisons with experiments or quantal calculations.

In almost any practical calculation, it is more convenient to deal with smooth constraining potentials instead of sharp inequalities; such potentials are also consistent with the probabilistic nature of quantum mechanics. Thus the quasiclassical Hamiltonian can be written

$$H_{\rm qc} = H_0 + V_H + V_P \ , \tag{1}$$

where

$$H_0 = E_{\rm kin} + E_{\rm Coul} \tag{2}$$

is the usual Hamiltonian, consisting of the kinetic energy

$$E_{\rm kin} = \sum_i \frac{1}{2m} p_i^2 \tag{3}$$

and interparticle Coulomb potentials

$$E_{\rm Coul} = -\sum_i \frac{Ze^2}{r_i} + \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \frac{e^2}{r_{ij}} \tag{4}$$

(m is the electron mass, $-e$ is the electron charge, and Ze is the nuclear charge), and V_H and V_P are momentum-dependent classical potentials introduced to represent nonclassical effects

$$V_H = \sum_i v_H(r_i, p_i) \tag{5}$$

and

$$V_P = \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \delta_{s_i,s_j} v_P(r_{ij}, p_{ij}) \tag{6}$$

with $\delta_{s_i,s_j} = 1$ if the spins of the ith and jth electrons are the same and 0 if they are different. For the constraints, KW suggested the form

$$v_c(r,p) = r^{-2} f(rp) \tag{7}$$

($c = H$ or P) and, in particular,

$$v_c(r,p) = \frac{(\xi_c \hbar)^2}{4\alpha r^2 m} \exp\left\{\alpha\left[1 - \left(\frac{rp}{\xi_c \hbar}\right)^4\right]\right\}, \tag{8}$$

where α is a hardness parameter determining how abruptly the constraint $rp \geq \xi_c \hbar$ is enforced. Note that $H_{\rm qc}$ is invariant under *separate* rigid-body rotations of the $\mathbf{r}_i$ and $\mathbf{p}_i$.

We can rearrange (1) in terms of one- and two-electron operators

$$H_{\rm qc} = \sum_i h_i^{(1)} + \frac{1}{2} \sum_i h_i^{(2)}, \tag{9}$$

where

$$h_i^{(1)} = \frac{1}{2m} p_i^2 - \frac{Ze^2}{r_i} + v_H(r_i, p_i) \tag{10}$$

and

$$h_i^{(2)} = \sum_{j(\neq i)} \left(\frac{e^2}{r_{ij}} + \delta_{s_i,s_j} v_P(r_{ij}, p_{ij}) \right) . \tag{11}$$

For comparison with quantities frequently reported in Hartree-Fock calculations, we define the "single-electron energy" (analogous, in the minimum-energy configuration, to the orbital energy, which is the Hartree-Fock eigenvalue [14])

$$\epsilon_i = h_i^{(1)} + h_i^{(2)} \tag{12}$$

and the "*total* single-electron energy" (analogous to the *total* orbital energy [15])

$$\eta_i = h_i^{(1)} + \frac{1}{2} h_i^{(2)} . \tag{13}$$

The ϵ_i is the energy of electron i in the field determined by all other particles. The less frequently mentioned η_i satisfies

$$H_{\rm qc} = \sum_i \eta_i . \tag{14}$$

Note that the constraint potentials Eq. (7) depend only on the product rp, except for the r^{-2} prefactor; this prefactor causes the constraints to scale like the kinetic energy and enables the minimum-energy configuration, at which $H_{\rm qc} = E_{\rm tot}$, to satisfy a modified virial theorem [8]

$$-E_{\rm Coul} = 2(E_{\rm kin} + V_H + V_P), \tag{15a}$$

which, using

$$E_{\rm tot} = E_{\rm Coul} + E_{\rm kin} + V_H + V_P \, , \tag{15b}$$

can be rewritten in the usual form [16]

$$E_{\text{Coul}} = 2E_{\text{tot}} \ . \tag{15c}$$

This relation provides some test of the minimization, though the condition is also satisfied at any local minimum.

The KW formulation is inherently a Hamiltonian description. That is, $p \neq \partial L/\partial \dot{r}$, where L is a Lagrangian corresponding to H_{qc} (actually it is awkward even to define this Lagrangian). The variable p is not the usual kinetic momentum; this is obvious from the fact that, *in the quasiclassical ground state*, r and p both have fixed (within symmetry operations) *nonzero* values satisfying $rp \approx \xi_H \hbar$, but nonetheless $d\mathbf{r}/dt = 0$. This seemingly strange state of affairs is not really a problem for two reasons: first, the purpose of the constraining potentials is simply to avoid quantum-mechanically forbidden regions of phase space, and second, p approaches the kinetic momentum for $rp \gg \xi_H \hbar$. As energy is supplied (by collisions or external fields) the particles move and at most times are little affected by the constraining potentials. Still, the constraining potentials provide the vital service of avoiding rare, but potentially catastrophic, excursions into regions excluded by quantum mechanics.

We retain the value of the stiffness parameter $\alpha = 5$ that was suggested by KW. Cursory investigations with other values showed that the *qualitative* structure is not sensitive to the value as long as it is not made too small. The problem with very large values ($\gtrsim 100$) is numerical in nature; encountering the resulting very large derivatives sometimes caused anomalous behavior by a given minimization routine and such problems may be expected to become even more troublesome for integration of dynamical equations of motion. On the other hand, very small values ($\lesssim 1$) invalidate the constraint potential; even for the hydrogen atom, such small values introduce local minima having energies similar to that of the desired minimum, but with values of rp significantly different from $\xi_H \hbar$ (for large α, there exists a relative minimum with $rp \approx 0$, but its energy is so high that it is of no consequence). In the search for the ground states, we found that the choice $\alpha = 5$ accommodates the numerical minimization by being small enough to yield a smooth function, but large enough to eliminate pronounced *unphysical* relative minima.

Following KW we choose the value of the Heisenberg parameter χ_H to yield the correct binding energy of hydrogenic atoms. For $\alpha \to \infty$, this value would be $\chi_H^\infty = 1.0$, but for finite α needs to be $\chi_H = \chi_H^\infty/(1 + \frac{1}{2\alpha})^{1/2}$ (≈ 0.9535 for $\alpha = 5$) to still give the right energy. Again following KW, we take $\chi_P^\infty = 2.767$, scaled to $\chi_P = \chi_P^\infty/(1 + \frac{1}{2\alpha})^{1/2}$ (≈ 2.6382 for $\alpha = 5$), which reproduces the Fermi energy of a close-packed nearest-neighbor electron-gas model.

Another approach, which has not been tried, might be to choose different χ_H and χ_P for each subject, such that each has the correct energy (or other properties). Problems with this alternative approach are that then the relevant parameters would change as atoms ionized in dynamical calculations and that the parameters might be different for atoms or ions with the same number of electrons but different nuclear charges. Besides, as we shall see, the single pair of parameters given in the preceding paragraph do an amazing job, at least on the average, throughout the Periodic Table.

B. Numerical minimization

Finding the quasiclassical ground-state configuration for an N-electron atom requires minimization of Eq. (1), which is a function of $6N$ variables. Because of the rotational invariances, this reduces to 2 independent variables for $N = 1$ (the magnitudes r and p) and $6N - 6$ independent variables for $N > 1$. This is a nontrivial minimization problem for a fairly large number of variables (e.g., 222 for $N = 38$). The main difficulty is in avoiding (or escaping) local minima which are numerous in the high-dimensional energy surfaces. All the minimization methods given in Ref. [17] were tried; one of these methods — the variable-metric (or quasi-Newton) method — emerged as clearly superior both in speed and avoiding spurious local minima.

The basic idea of the variable-metric (VM) method is to iteratively approximate the inverse of the Hessian matrix $\mathbf{A}$, whose components are the second partial derivatives of the function $f(\mathbf{x})$ to be minimized. It is assumed that the function $f(\mathbf{x})$ can be locally approximated by a quadratic form so that

$$\boldsymbol{\nabla} f = \mathbf{A}\mathbf{x} - \mathbf{b} \ . \tag{16}$$

Hence

$$\mathbf{x}_{\min} = \mathbf{A}^{-1}\mathbf{b} \ , \tag{17}$$

but we do not know $\mathbf{A}$ or $\mathbf{b}$ at the outset. The method requires analytic evaluation of first derivatives.

In each iteration (starting with $\mathbf{A}_0$ equal to the unit matrix) the function of f is minimized in the *direction* of $\mathbf{A}_i \boldsymbol{\nabla} f(\mathbf{x}_i)$, where $\mathbf{x}_i$ is the estimate of $\mathbf{x}_{\min}$ and $\mathbf{A}_i$ is the estimate of $\mathbf{A}$ at the ith iteration, to determine $\mathbf{x}_{i+1}$. A new approximation $\mathbf{A}_{i+1}$ to $\mathbf{A}$ is also determined satisfying

$$\mathbf{x}_{i+1} - \mathbf{x}_i = \mathbf{A}_{i+1}[\boldsymbol{\nabla} f(\mathbf{x}_{i+1}) - \boldsymbol{\nabla} f(\mathbf{x}_i)] \ . \tag{18}$$

Though this equation does not uniquely specify $\mathbf{A}_{i+1}$, the exact choice of $\mathbf{A}_{i+1}$ is of some importance. For this purpose, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was employed (see [18] for details). A key property of the method is the search in conjugate directions $\mathbf{A}_i \boldsymbol{\nabla} f(\mathbf{x}_i)$; this means that the exact $\mathbf{x}_{\min}$ and $\mathbf{A}^{-1}$ of a quadratic function of n variables will require at most n iterations [19] — thus the name "quasi-Newton." Of course, the actual function is not globally quadratic.

Though the convergence properties are generally good, the VM BFGS method does not always converge to the correct global minimum for every choice of $\mathbf{x}_0$. Thus we perturb the solution and carry out the minimization repeatedly until this result has been confirmed several times. An efficient procedure for minimizing the energy

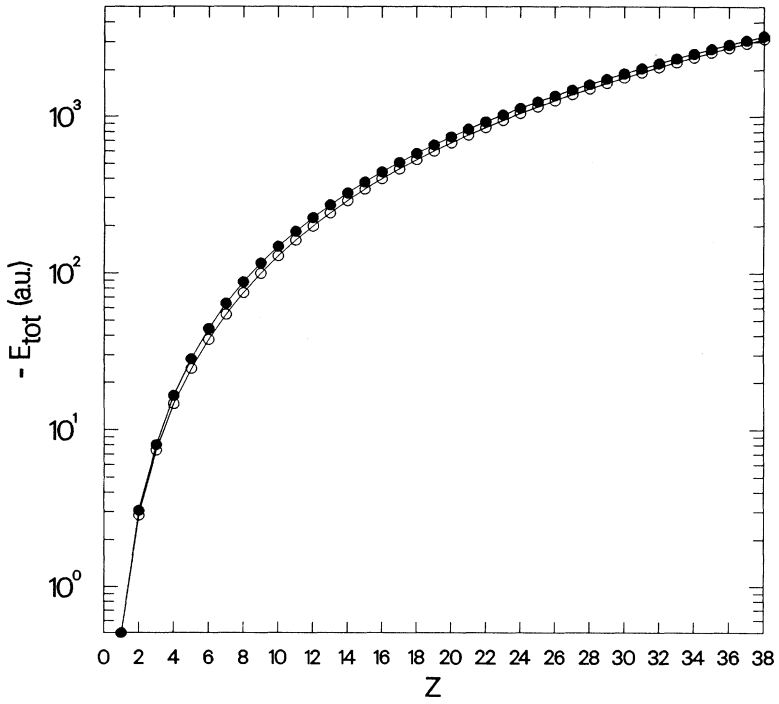

FIG. 1. Total quasiclassical energies (closed circles) compared with Hartree-Fock energies [23] (open circles) of neutral atoms.

of atoms with large numbers of electrons was found to be starting with the optimized result of a smaller atom as the initial condition for its core configuration. Usually this procedure led directly to the optimum configuration of the next-larger atom. However, in order to allow for the possibility that addition of the electron might lead to a new minimum of the N-electron atom in which the inner electrons are rearranged from that of the $(N-1)$-electron atom, additional calculations were done in which up to six electron configurations were randomly changed in the initial condition. In the results it will be seen that such rearrangements are unusual, but do occur. Multiple trials and checks of required physical conditions help confirm that the found minimum is global, but there can be no absolute guarantee in general.

For general interest, we mention a quite different ap-

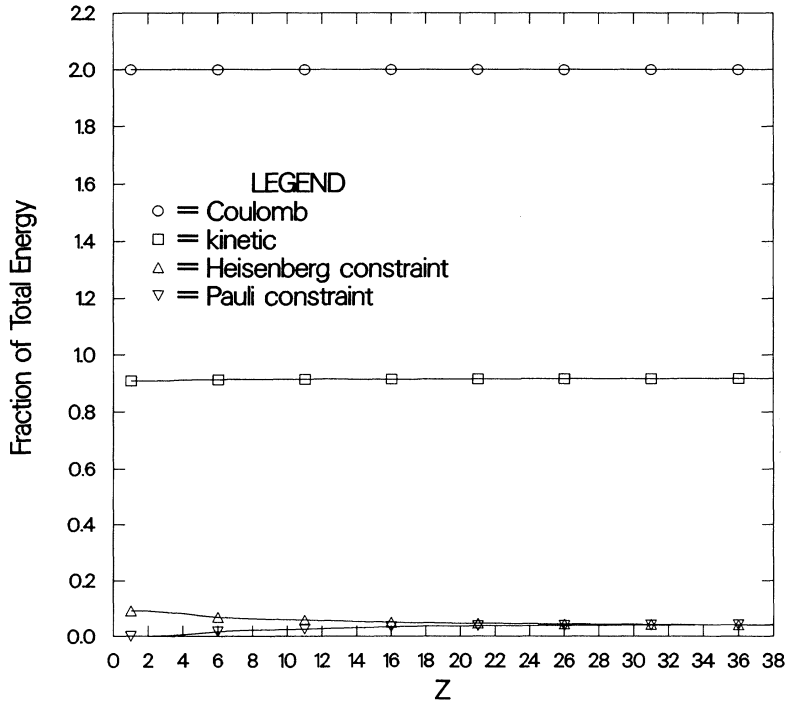

FIG. 2. Fractional Coulomb, kinetic, and constraint (Heisenberg and Pauli) contributions to the total quasiclassical energies of neutral atoms. The Coulomb energy is negative, the others positive. The values were calculated at every Z though, for clarity, not every point is marked by a symbol.

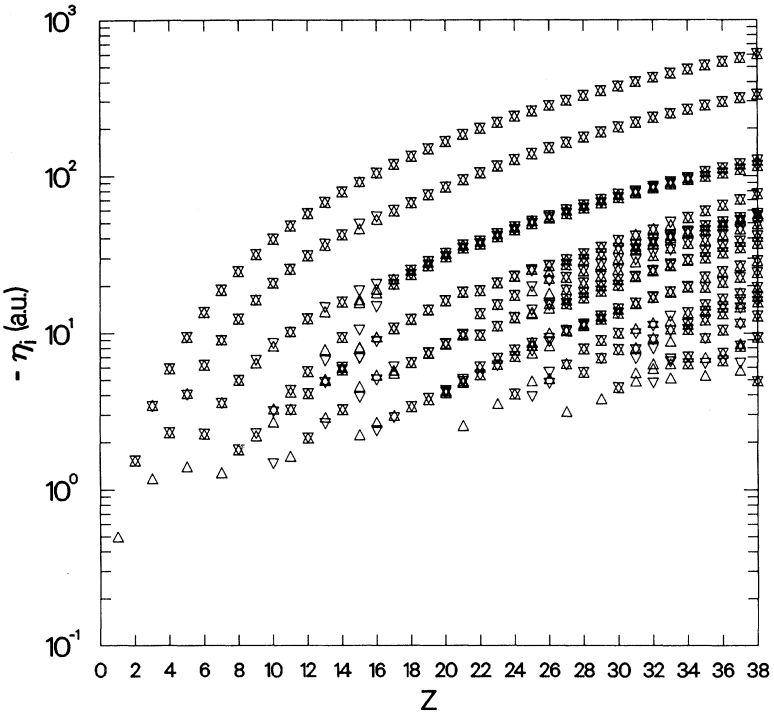

FIG. 3. Total single-electron quasiclassical energies (negative) for neutral atoms $-\eta_i$ for $i = 1$ to Z [see Eq. (13)]. Upward (downward) -pointing triangles are for α (β) -spin electrons.

proach, *simulated annealing*, which has been successful in finding global minima of other physical functionals. Both the standard version [17], adapted to a function of continuous variables, and the hybrid downhill simplex-simulated annealing method [20] were tried, but without notable success. With reasonable annealing choices, the searches were found to be extremely time consuming and to often get stuck in local minima. Success of this procedure can depend on rearrangement of the independent variables and whether the independent variables are changed singly or jointly; several strategies were tried, but it may well be that a more effective choice was missed.

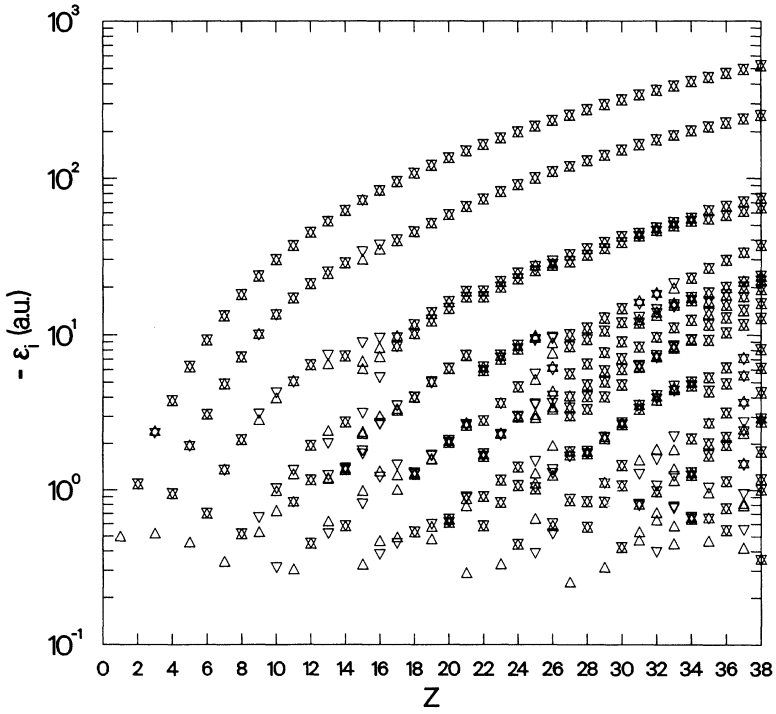

FIG. 4. Single-electron quasiclassical energies (negative) for neutral atoms $-\epsilon_i$ for $i = 1$ to Z [see Eq. (12)]. Upward (downward) -pointing triangles are for α (β) -spin electrons.

III. RESULTS

Calculations were done on all atoms and singly charged ions with $Z = 1$ to 38. The calculations were done both (i) with the electron coordinates and momenta completely free (except, as permitted by spatial isotropy, the first vector is placed along the z axis and the second vector is in the x-z plane) and (ii) with the electrons constrained into pairs having $\mathbf{r}^{(\beta)} = -\mathbf{r}^{(\alpha)}$ and $\mathbf{p}^{(\beta)} = -\mathbf{p}^{(\alpha)}$. The latter treatment halves the number of variables (for N even) and is somewhat akin to the restricted Hartree-Fock method of quantum mechanics. However, we shall see that the "correlation" energy defined by this quasiclassical ansatz differs considerably from the customary value. All of the results presented below are for unpaired electrons, except when the correlation is being discussed.

The total quasiclassical energies are shown in Fig. 1, where they are compared with the accurate nonrelativis-

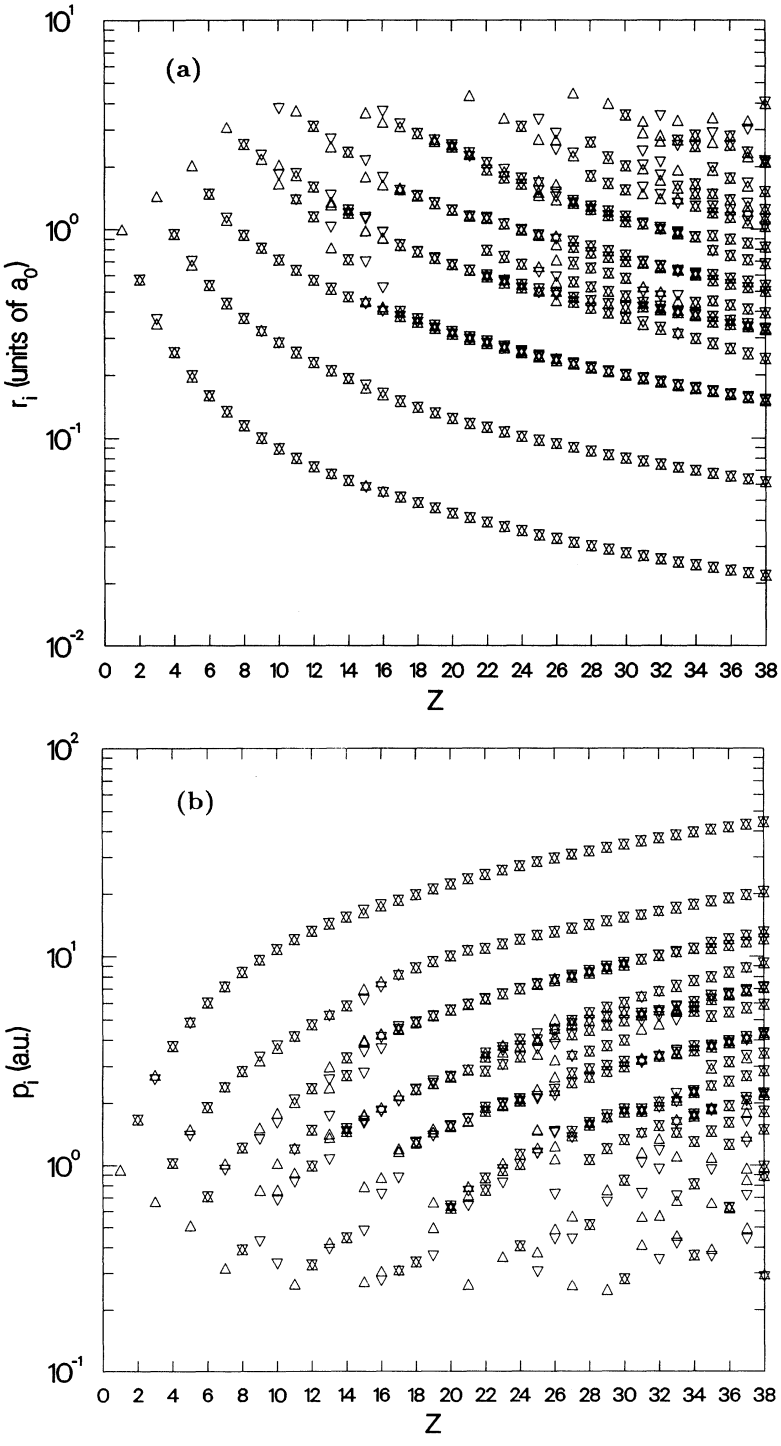

FIG. 5. (a) Distances r_i from the nucleus and (b) momenta p_i of quasiclassical electrons in the ground-state configuration, $i = 1$ to Z. Upward (downward) -pointing triangles are for α (β) -spin electrons.

tic Hartree-Fock energies (average energy of configuration). The agreement is remarkably good. In all cases, the quasiclassical binding is slightly greater than the true binding energy (except H, where the energies are identical by design). This direction of the small disagreement is as expected since the quasiclassical ground state has no zero-point energy.

It is also of interest to look at the separate terms. The kinetic, Coulomb, and constraint contributions to the total energy in the minimum-energy configuration are shown in Fig. 2. The virial condition $E_{\mathrm{Coul}} = 2E_{\mathrm{tot}}$ is precisely satisfied. It can be seen that the sum of the two constraint energies is about 8% of the total energy and is only weakly dependent on Z, decreasing slowly. At $Z < 35$, the Pauli energy, which is zero for H and He, is smaller than the Heisenberg energy; at higher Z, the Pauli energy becomes the larger of the two. The fraction of the total energy due to the constraints is approxi-

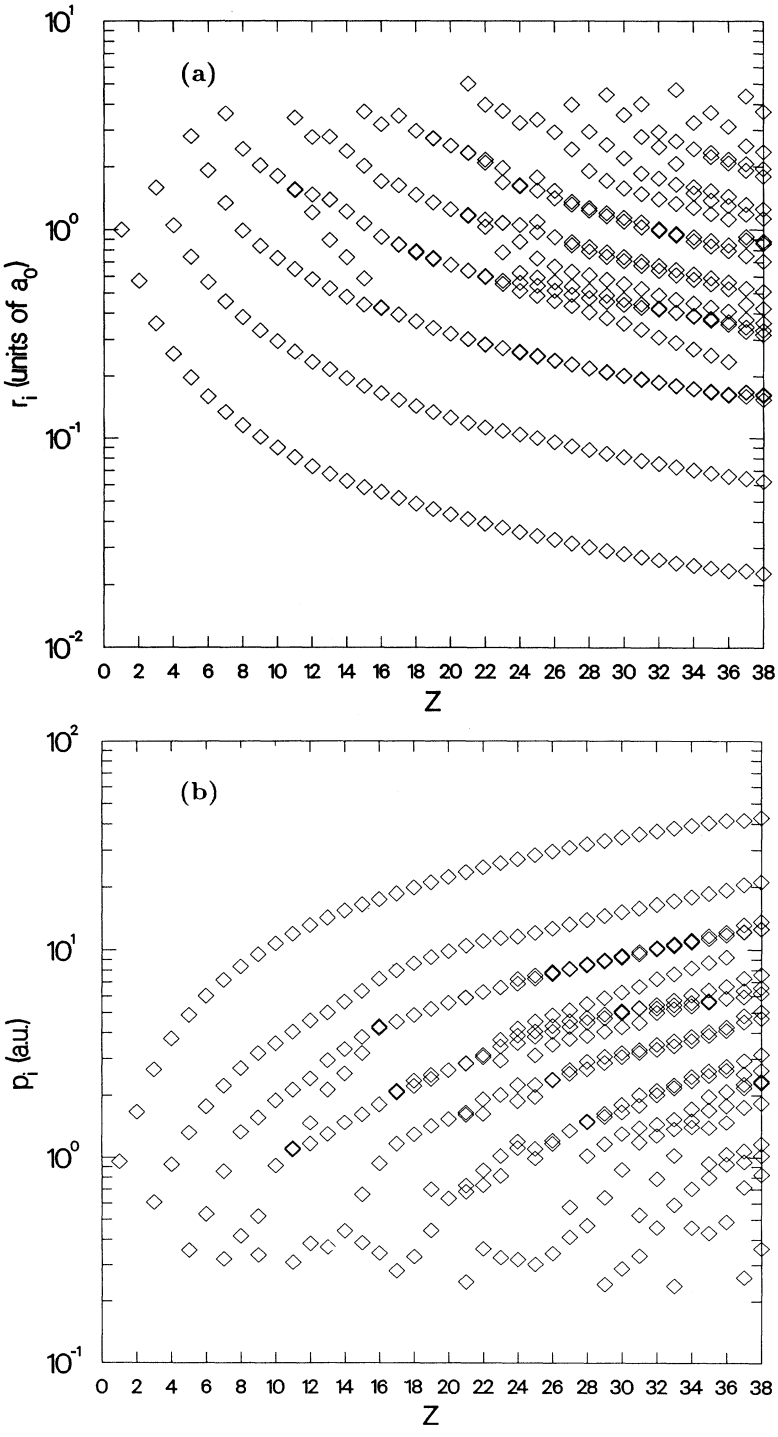

FIG. 6. (a) Distances from the nucleus and (b) momenta of electrons in the ground-state configuration resulting from forced electron pairing. Each diamond symbol represents an electron pair, except the last (r_Z, p_Z) in the case of odd Z. Doubled pairs are seen as bolder (slightly offset) diamonds.

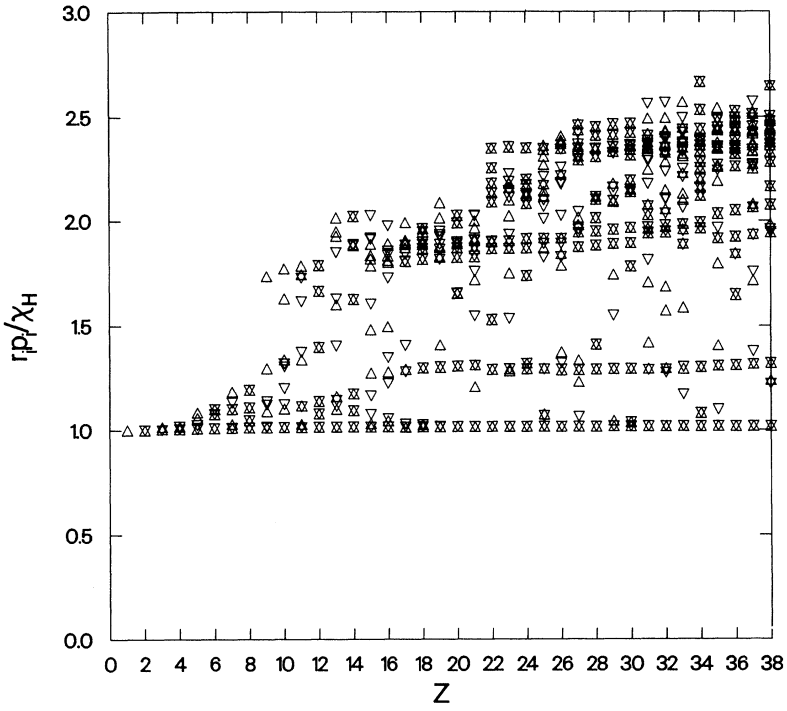

FIG. 7. Heisenberg constraint parameters $r_i p_i/\chi_H$ for the ground-state configurations. Upward (downward) -pointing triangles are for α (β) -spin electrons.

mately inversely proportional to the hardness parameter α.

The total single-electron energies η_i are shown in Fig. 3 and the single-electron energies ϵ_i are shown in Fig. 4. By Koopmans's theorem [21],

$$\epsilon_i^{(N)} = E_{\rm tot}^{(N)} - E_{\rm tot}^{(N/i)}, \tag{19}$$

where the superscript (N) designates the N-electron atom in its minimum-energy configuration and (N/i) designates the *same* configuration except with the ith electron removed to infinity. Thus the ϵ_i give the ionization potentials in the approximation that no rearrangement occurs in the aftermath of the ionization. A comparison with the actual quasiclassical ionization potentials is made below.

The quasiclassical shell structure is most easily visu-

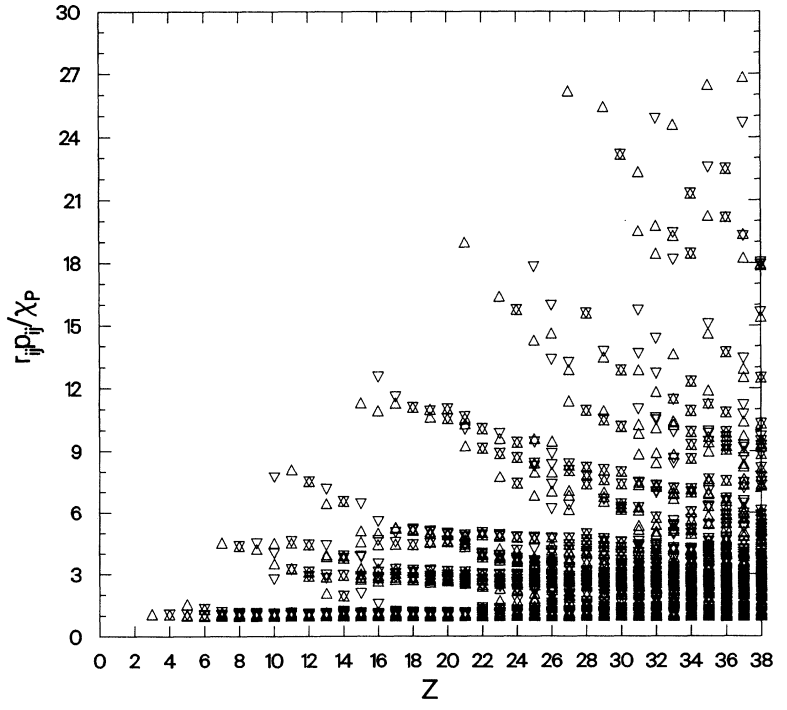

FIG. 8. Pauli constraint parameters $r_{ij}p_{ij}/\chi_P$ for electrons of the same spin (upward-pointing triangles for α, downward-pointing triangles for β) in the ground-state configurations.

alized by examining the magnitudes of the electron distances r_i and momenta p_i relative to the nucleus. The r_i and p_i for all the electrons of neutral atoms with $1 \leq Z \leq 38$ are shown in Figs. 5(a) and 5(b). In these figures the α and β electrons are distinguished by upward- and downward-pointing triangles, respectively. A strong tendency for α and β electrons to pair is evident, but is not inviolate — the exceptions are not numerical artifacts. There is a weaker tendency for the shells, outside

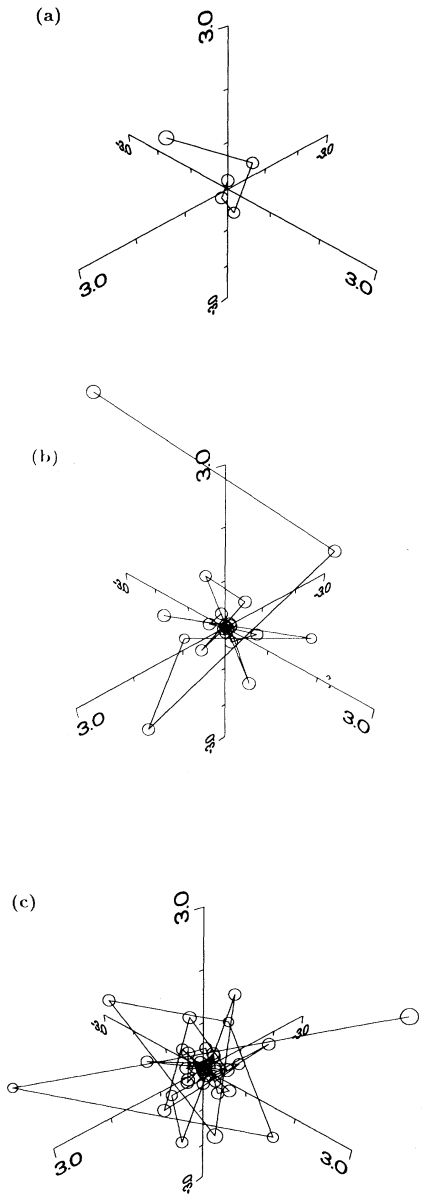

FIG. 9. Perspective plots of quasiclassical electrons in their ground-state configuration: (a) $Z = 5$, $N = 5$, (b) $Z = 21$, and $N = 21$, and (c) $Z = 38$, $N = 38$. The vantage point for the view is $x = y = z = 5a_0$.

TABLE I. Positions and momenta of quasiclassical electrons for minimum-energy configurations of atoms with $1 \leq Z \leq 8$.[a] Angles are given in radians. The parameters are $\chi_H = 0.9535$, $\chi_P = 2.6382$, and $\alpha = 5$. The positions and momenta are independently invariant under rigid-body rotations.

r (a_0)	θ_r	ϕ_r	p (a.u.)	θ_p	ϕ_p	Spin
		$Z = 1$				
1.0000	0.0000	0.0000	0.9535	0.0000	0.0000	α
		$Z = 2$				
0.5714	0.0000	0.0000	1.6686	0.0000	0.0000	α
0.5714	3.1416	0.0000	1.6686	3.1416	0.0000	β
		$Z = 3$				
0.3506	0.0000	0.0000	2.7291	0.0000	0.0000	α
0.3673	2.6567	0.0000	2.5962	3.1416	0.0000	β
1.4419	2.2031	3.1416	0.6716	3.1416	0.0000	α
		$Z = 4$				
0.2565	0.0000	0.0000	3.7332	0.0000	0.0000	α
0.2565	2.3683	0.0000	3.7332	2.5673	0.0000	β
0.9458	2.7593	2.3378	1.0256	3.1416	0.0000	α
0.9458	1.0666	3.4534	1.0256	0.5743	3.1416	β
		$Z = 5$				
0.1961	0.0000	0.0000	4.8987	0.0000	0.0000	α
0.1988	2.2549	0.0000	4.8261	2.5672	0.0000	β
0.6736	2.8938	3.1416	1.4993	3.1416	0.0000	α
0.7008	1.1318	3.1416	1.3944	0.5743	3.1416	β
2.0196	0.6731	0.0000	0.5121	0.0000	0.0000	α
		$Z = 6$				
0.1599	0.0000	0.0000	6.0156	0.0000	0.0000	α
0.1599	2.1806	0.0000	6.0156	3.1416	0.0000	β
0.5361	2.9180	3.1416	1.9150	3.1416	0.0000	α
0.5361	1.1846	3.1416	1.9150	0.0000	0.0000	β
1.4800	0.2338	0.0000	0.7091	0.0000	0.0000	α
1.4800	1.9468	0.0000	0.7091	3.1416	0.0000	β
		$Z = 7$				
0.1335	0.0000	0.0000	7.2132	0.0000	0.0000	α
0.1344	2.1402	0.0000	7.1645	2.9800	0.0000	β
0.4373	2.9439	3.1416	2.4004	3.1416	0.0000	α
0.4405	1.1921	3.1416	2.3820	0.1616	3.1416	β
1.1068	0.2777	0.0000	1.0209	0.0000	0.0000	α
1.1332	1.9071	0.0000	0.9524	2.9800	0.0000	β
3.0842	2.2428	3.1416	0.3182	3.1416	0.0000	α
		$Z = 8$				
0.1147	0.0000	0.0000	8.4039	0.0000	0.0000	α
0.1147	2.1162	0.0000	8.4039	3.1416	0.0000	β
0.3718	2.9653	3.2059	2.8408	3.1416	0.0000	α
0.3718	1.2014	3.1295	2.8408	0.0000	0.0000	β
0.9348	0.3020	0.4786	1.2168	0.0000	0.0000	α
0.9348	1.8438	6.1405	1.2168	3.1416	0.0000	β
2.5510	2.1970	4.2811	0.3908	3.1416	0.0000	α
2.5510	1.5563	2.3144	0.3908	0.0000	0.0000	β

[a]These and all other configurations — for $Z = 1$ to 38, atoms and ions, unpaired and force-paired calculations — are available electronically. The following procedure can be used to access the files using the UNIX ftp utility: (1) ftp t4.lanl.gov; (2) log in with name anonymous; (3) cd pub/cohen/quasiclassical; (4) get *filename* where *filename* is atoms.unpair, atoms.pair, or readme — additional information is provided in the file readme; (5) quit when finished. Send electronic-mail inquiries to cohen@lanl.gov

the first two with two electrons each, to consist of four electrons. This grouping is somewhat more evident in Figs. 6(a) and 6(b), which are the results of calculations in which pairing of α and β electrons was forced. Back in Fig. 5 a few "broken-symmetry" cases can be spotted where a shell appears to consist of an odd number of electrons; one of these, $Z = 10$, confirms the finding in the original paper of Kirschbaum and Wilets [8]. The occasional structural reversals seen as Z increases is reminiscent of anomalies occurring in filling the $3d$ shell of real transition-metal atoms.

In Fig. 7 the values of $r_i p_i/\chi_H$, which prevent classical collapse into the nucleus via the effective Heisenberg potential, are shown for the minimum-energy configurations. The essential role of χ_H for the first pair of electrons is clear from its unit value for these electrons. For more weakly bound electrons, the value increases — and the constraining potential decreases $\sim \exp[-\alpha(r_i p_i/\chi_H)^4]$ — as the roles of electron-electron Coulomb repulsion and the effective Pauli potential become more important. The analogous values of $r_{ij} p_{ij}/\chi_P$ for the Pauli potential are shown in Fig. 8. The effect of the χ_P parameter on shell structure is evident by the increasing number of values close to unity as Z increases.

Three-dimensional perspective visualizations of the quasiclassical atoms with 5, 21, and 38 electrons are shown in Figs. 9(a)–9(c). The classical snapshot shows a single set of "point" particles, but, of course, in any application the rotational invariance should be taken into account, e.g. by use of an ensemble of orientations. The ground-state configurations for $1 \leq Z \leq 8$ are given in Table I; all are available electronically (see the footnote in Table I).

Since ionization is one of the the main classes of problems where the quasiclassical model is expected to be useful, the ionization potentials are of some importance. From the accuracy of the total energies we know that the average of all the ionization potentials is fairly accurate, but the first ionization potential provides a more stringent test. Independent calculations were performed on all ions with $N = Z - 1$. The resulting ionization potentials are compared with the accurate values for real atoms in Fig. 10. On the average they are not too bad, though there are a few, such as neon, which was already pointed out for its anomalous triplet shell, that fail more seriously. A comparison with the single-electron energies ϵ_i is made in Fig. 11. Generally the single-electron energies provide reasonable approximations to the ionization potentials, though in some cases they are as much as a factor of 2 larger — always larger since relaxation can only lower the energy of the ion.

Finally we look at the energy consequence of electron pairing. Figure 12 shows the energy difference (per electron) between calculations done with forced pairing and with all electrons free. Though this would appear to be conceptually similar to the quantum-mechanical concept of electron correlation, the quasiclassical energy is zero for helium and about six times larger than the quantal value [24] (which is ~ 0.04 a.u./electron) for $Z > 8$. Evidently correlation effects between the point quasiclassical particles are considerably more important than for diffuse orbitals.

IV. CONCLUSIONS

We have determined the ground-state configurations for the Kirschbaum-Wilets quasiclassical atoms having

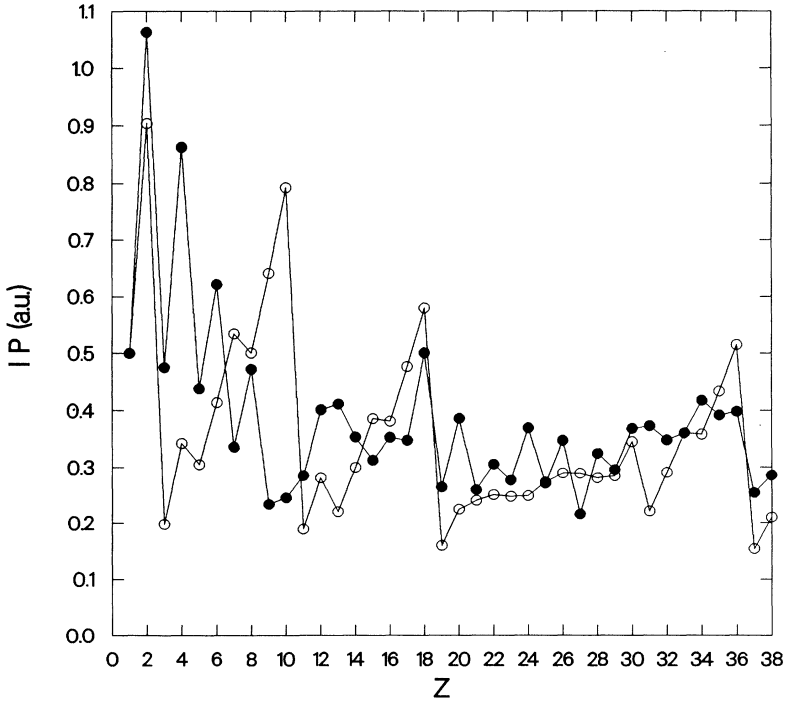

FIG. 10. Quasiclassical ionization potentials (closed circles) compared with experimental ionization potentials [22] (open circles).

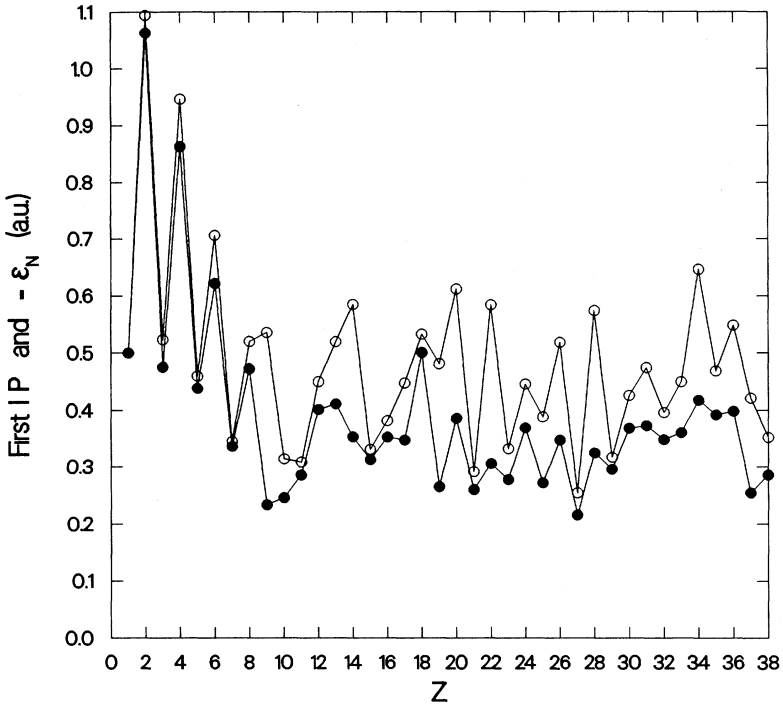

FIG. 11. First quasiclassical ionization potentials (closed circles) compared with smallest (in magnitude) single-electron energies (open circles).

$1 \leq Z \leq 38$. Still higher Z could be equally well calculated, though in practice the inner electrons would then probably be replaced by an effective core potential for most applications. The model is formulated with an effective Hamiltonian from which classical equations of motion can be determined. The only parameters occurring in the model are two constants representing the quantum-mechanical effects of the Heisenberg and Pauli principles and the associated hardness parameters determining how abruptly these constraints are implemented. The parameters originally suggested by KW [8] were found to be quite adequate and, for a general model allowing changes in ionization stage or nuclear charge, it was deemed undesirable to fiddle with the parameters of each species to

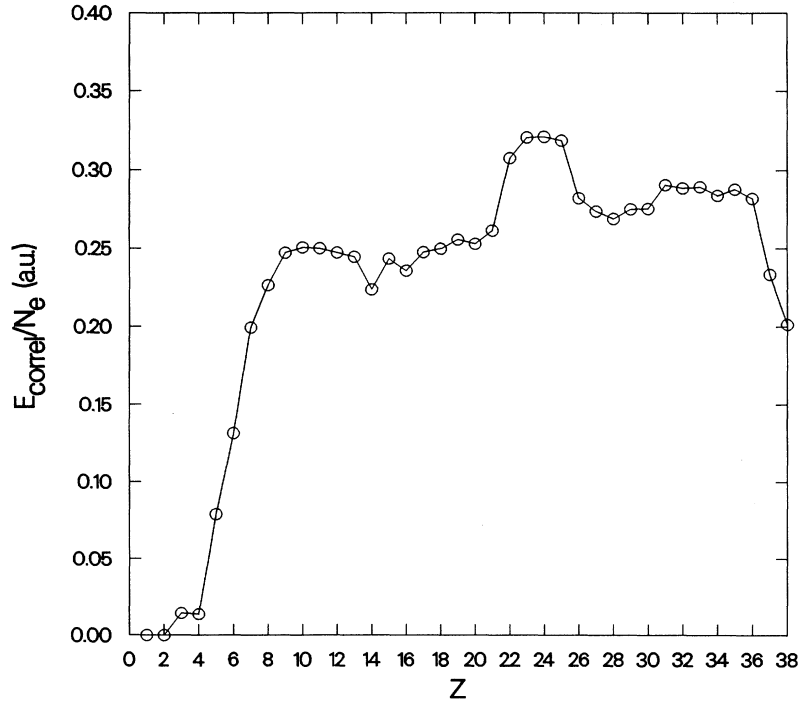

FIG. 12. Quasiclassical "correlation energies" per electron (see text) of neutral atoms.

make marginal improvements in the atomic properties. The total electronic energies are given rather accurately and the first ionization potentials are about right on the average, though they do not generally peak at the noble-gas atoms.

In addition to providing a stable atomic structure, this quasiclassical model — in contrast to the Thomas-Fermi model — displays a shell structure. However, unlike the real atomic shells of $2N^2$ electrons, the KW quasiclassical shells generally all contain two or four electrons. Presumably this inadequacy is due to the static (crystalline) nature of the ground state; the effective potentials depend only on the relative linear momenta, but not on the angular momenta, which play an essential role in determining the real shell structure. Of course, angular momentum will be properly conserved as energy is added (by field or collisions) to the crystalline ground state and it may be fruitful to consider how its effects could be taken into account even for the initial state.

In considering refinements of the model, it is important to keep in mind that the goal is a useful method for practical calculations of correlated motions in collisions or external fields. Some improvements, e.g., allowing electrons to be diffuse, would probably negate the overall utility of the model. One generalization, which perhaps should be considered, is taking zero-point energy into account. For a quasiclassical atom subject to strong excitation, the zero-point motion is likely negligible, but for near-static properties it may be essential.

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