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Semiclassical Nature of Planetary Atom States

The semiclassical quantization of classically stable planetary atom configurations (the so-called frozen planet configurations) is discussed in some detail. The existence of (approximate) integrals of motion allows for a torus quantization procedure, the semiclassical limit of which is the Gutzwiller periodic orbit formula reduced to fundamental orbits only. We show that the multi-dimensional torus quantization yields accurate semiclassical energies for the planetary atom states. We compare our results with those obtained by a multipole model of the electron–electron interaction which has been proposed as a more transparent model for describing the frozen planet configurations. We give evidence that this model fails in predicting the energies for large quantum numbers.

Key Words: *planetary atoms, semiclassical quantization, multipole expansions*

I. INTRODUCTION

The non-separability of the electron pair motion in the helium atom, described by the Hamiltonian

$$H = \frac{\mathbf{p}_1^2}{2} + \frac{\mathbf{p}_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \tag{1}$$

with the nuclear charge $Z = 2$, becomes evident in the case of high double excitation, where the electron–electron interaction $1/r_{12}$ is of comparable importance to the electron–nucleus interaction Z/r_i, $i = 1, 2$. The electron correlation leads to the breakdown of independent particle approaches and has focused interest on the search for approximate symmetries using collective coordinates of the three particles. Progress has been made in uncovering approximate

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symmetries for particular classes of states.[1–5] Even though the quantum numbers derived in the various approaches may be used to *label* all states they do not always describe the symmetries of the wavefunctions involved in that they do not always *count* nodal surfaces correctly.

Recently[6,7] (semi-) classical approach was proposed to describe a certain class of states, the so-called *frozen planet configurations* (FPC). These asymmetrically excited states are composed of a strongly polarized (inner) electron and an (outer) electron which is dynamically localized near some fixed radial distance. The character and the novel symmetries of these states were verified and analyzed in detail later.[5] The semiclassical analysis accumulated in a WKB-type formula for the energies of these states (in the following we focus on states with total angular momentum $\mathbf{L} = 0$),

$$\frac{S_{PO}}{\sqrt{-E_{nkl}}} = 2\pi\hbar\left(n + \frac{1}{2} + \left(l + \frac{1}{2}\right)\alpha_1 + 2\left(k + \frac{1}{2}\right)\alpha_3\right). \quad (2)$$

The semiclassical quantum numbers n, k, l reflect the approximate separability of the associated wavefunctions in local coordinates parallel and perpendicular to the periodic orbit: nodal excitations along the orbit are described by n, whereas k (bending motion) and l (transverse radial motion) count the excitations perpendicular to the orbit. Formula (2) contains properties of the fundamental periodic motion of the FPCs only, i.e., the action S_{PO} of the shortest periodic orbit (PO) calculated at the total energy $E = -1$ (the action for arbitrary energy E_{nkl} scales according to the left-hand side of Eq. (2)) and the energy independent winding numbers α_1, α_3 for the motion transverse to the orbit. For $l = k = 0$, Eq. (2) gives accurate results for the FPC states which turn out to be the lowest states of the energetically highest two-electron Rydberg series $N_1 = n + 1$, $N_2 \to \infty$ converging to the N_1 threshold of the He^+ ion. Even more important, it was shown that the energies (2) are exact in the semiclassical limit $E \to 0$, i.e., $n \to \infty$.[5,8] Despite the very simple appearance and the success of the formula (2), the semiclassical approach was criticized harshly in the literature.[9,10]

The major criticism concerns the fact that the formula fails for k, $l \to \infty$ (but n fixed!) and that the energies do not converge to a

single-particle escape threshold for either $l \to \infty$ or $k \to \infty$.[9–11] However, it was emphasized in Refs. 5 and 8 that the formula accurately describes only those states which are localized in the vicinity of the periodic orbit, i.e., $k, l \ll n$. The Gutzwiller trace formula[12] from which Eq. (2) is derived implies a non-symmetrical treatment of the quantum numbers n and k, l in that it approximates the action accumulated by the motion transverse to the periodic orbit only to leading order, i.e., harmonically in the coordinates perpendicular to the orbit. In the present Comment we argue that the criticisms are insubstantial for a full semiclassical torus quantization of which the Gutzwiller approximation (2) is the asymptotic limit $n \gg k, l$.[13]

II. CLASSICAL ANALYSIS

The frozen planet configurations (FPC) consist of an electron pair located (predominantly) on the same side of the atom.[6] The inner electron 2 moves on slightly perturbed Kepler ellipses with slowly varying major axes. The outer electron 1 follows the slow precession of the inner electron whereas its radial coordinate r_1 oscillates according to an effective potential well formed by the asymptotically ($r_1 \to \infty$) dominant nuclear attraction and the electron–electron repulsion at short interelectron distances. The repulsive component prevents the outer electron from penetrating into the region close to the nucleus.

For vanishing total angular momentum $\mathbf{L} = 0$, the purely *collinear* FPC covers a lower-dimensional invariant part of the full phase space. The corresponding energy-shell $H = E = \text{const.}$ is three-dimensional and its structure is conveniently visualized by taking Poincaré surfaces of sections (SOS).[5] In Fig. 1 the phase space position $\{r_1, p_1\}$ of the outer electron of the helium atom is monitored each time the inner electron approaches the nucleus ($r_2 = 0$). Obviously, the phase space foliates in invariant tori and the electron pair motion is near-integrable and regular. Near the central fixed point the motion of the outer electron is quasi-harmonic, but for large r_1 the elongated tori mirror an almost Keplerian motion of the outer electron. The open manifolds surrounding the closed tori represent regular trajectories for which the outer electron ionizes.

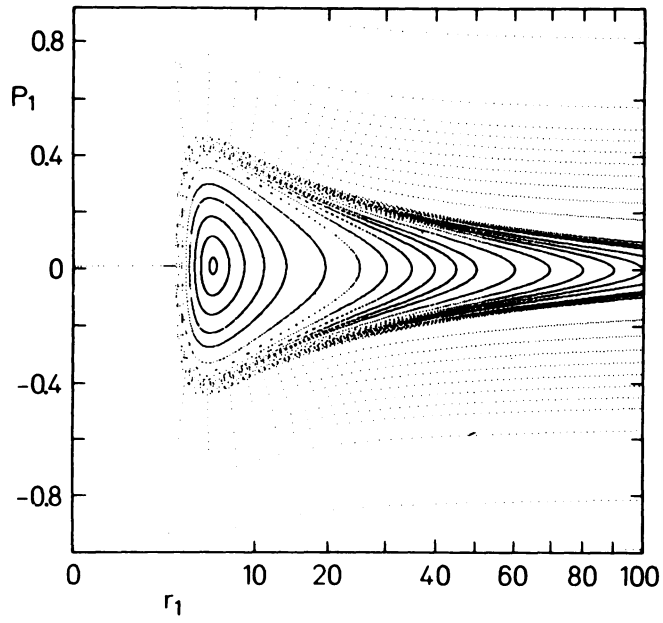

FIGURE 1 Poincaré surface of section ($r_2 = 0$) for collinear configurations with both electrons on the same side of the nucleus ($Z = 2$, $E = -1$).

If the initial distance is smaller than a critical value, $r_1 \approx 5$ in the SOS, the outer electron will ionize immediately, i.e., its radial distance r_1 increases in the SOS for all times.

The periodic motion for which both electrons oscillate coherently with the same frequency appears as the central elliptic fixed point in the SOS. For this *fundamental periodic orbit* of the FPC the outer electron is *dynamically* localized near some fixed radial distance while the inner electron oscillates between the nucleus and its outer turning point. This pronounced localization gave rise to the labelling as frozen planet states.[6,14]

Remarkably, the fundamental PO is also stable with respect to variations of the initial conditions perpendicular to the symmetry plane of collinear motion, i.e., when the electrons move in a (slightly) off-collinear arrangement.[6] Therefore the PO is embedded in a fully six-dimensional island of stability in phase space.

It is also stable for finite angular momentum $L \neq 0$ as was shown in Ref. 15, where this type of electron motion was "rediscovered" and analyzed (their type-2 configuration).

It follows from the near-integrable nature of the FPC that *locally* a canonical transformation to action/angle variables can be found after which the Hamiltonian becomes approximately independent of the angle variables θ_i,[12] i.e.,

$$H(p_1, r_1, p_2, r_2, p_{12}, r_{12}) = H(J_1, J_2, J_3, \theta_1, \theta_2, \theta_3)$$
$$\approx H(J_1, J_2, J_3) \,. \tag{3}$$

The action variables J_1, J_2, J_3 measure the phase space area enclosed by the different independent circuits around the tori to which the motion is confined. The main information on the classical motion is then contained in a single energy-surface $H(J_1, J_2, J_3) = \text{const}$ in the (J_1, J_2, J_3)-action plane. The energy-surfaces for arbitrary (negative) energies are simply given by scaling the action coordinates. Unfortunately, there is no general procedure to derive the action (and conjugated angle) variables analytically. However, we will briefly outline how they can be determined numerically.[16] Approximately, J_1 represents the radial motion of the outer electron, J_2 the radial motion of the inner electron, and J_3 the bending degree of freedom. There are two linearly independent and equivalent directions for which bending can take place in space. For $L = 0$ the space fixed plane of the three particles determines one direction, the other being orthogonal to this plane and thus described by the Euler angles. For simplicity we restrict ourselves from now on to motion inside the symmetry plane of collinear motion ($J_1, J_2, J_3 \equiv 0$), but the method outlined below can be generalized in a straightforward way to $J_3 \neq 0$.

The total action J of a (not necessarily periodic) trajectory accumulated after one closure of the circuit 2 on the torus is given by

$$J(\alpha) = J_2 + \alpha J_1, \tag{4}$$

where the winding number α is given by the frequency ratio

$$\frac{\partial H/\partial J_1}{\partial H/\partial J_2} = \frac{\dot{\theta}_1}{\dot{\theta}_2} = \frac{\omega_1}{\omega_2} = \alpha \tag{5}$$

of the motion. For the central fixed point of Fig. 1 the winding number can be determined by a linear stability analysis of the corresponding PO, i.e., by the eigenvalues $\exp(\pm 2\pi i \alpha_{PO})$ of the orbit's stability matrix.[17] For the PO the dimension of the torus reduces by one and the phase space area enclosed by the circuit 1 vanishes, i.e.,

$$\left.\frac{dJ}{d\alpha}\right|_{\alpha_{PO}} = J_1 = 0, \quad J(\alpha_{PO}) = S_{PO}/\sqrt{-E} \tag{6}$$

with $S_{PO} = 1.491499$ and $\alpha_{PO} = 0.067650$.[5]

Orbits on tori with rational winding number $\alpha = r/s$ (r, s being integers) close themselves after s revolutions and are again periodic. For an exactly integrable system there is a continuously connected family of POs on the corresponding rational torus. However, even under an infinitesimal perturbation such a resonant torus will generally break up and only two POs survive (Poincaré–Birkhoff Theorem),[12] one of which is stable and one of which is unstable. With increasing perturbation strength the actions of these two orbits will differ. Their differences are a measure of the strength of the non-integrable part of the Hamiltonian neglected in Eq. (3).

We here use the actions of the POs to approximate the action functional (4) for rational tori. We find that the actions of the stable and unstable orbits differ by less than one part in 10^6 which is the accuracy with which we determine the action integrals numerically. In Fig. 2 we plot the actions of 43 different periodic orbits with a fitting function to be explained below. Obviously, the action functional becomes stationary at $\alpha = \alpha_{PO}$ and then decreases monotonically to $J = Z/\sqrt{-2E} = \sqrt{2}$ as $\alpha \to 0$.

To determine the action functional as $\alpha \to 0$ it is instructive to investigate the helium atom with the electron–electron interaction approximated by the monopole expansion, which is justified when the radial distances ($r_1 \gg r_2$) and periods ($\alpha = T_2/T_1 \to 0$) largely differ,

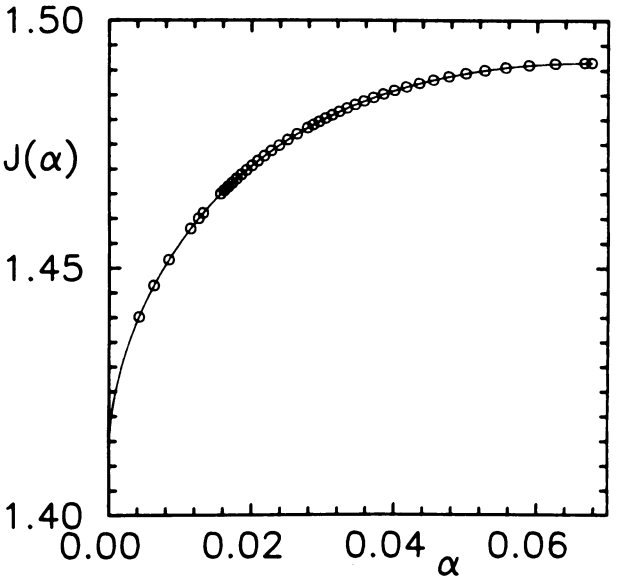

FIGURE 2 Accumulated actions of collinear periodic orbits (drawn as circles) after the first return to the SOS as a function of their winding number α. The solid line represents a semi-analytical fitting function.

$$H_M = \left(\frac{p_2^2}{2} - \frac{Z}{r_2}\right) + \left(\frac{p_1^2}{2} - \frac{Z-1}{r_1}\right). \tag{7}$$

By simply applying Kepler's laws one derives from Eq. (7) the action functional

$$J_M(\alpha) = \frac{Z}{\sqrt{-2E}}\left[1 + \left(\frac{Z-1}{Z}\alpha\right)^{2/3}\right]^{3/2}. \tag{8}$$

The monopole approximation, correct to leading order in α for the full problem, gives the calculated actions to an accuracy better than 10%. It does not, however, reflect the stationary behavior at α =

α_{PO} which is due to higher multipole components in the inter-electron potential. The simple ansatz

$$J_M + c_1 a + c_2 a^2, \tag{9}$$

however, can be used to enforce the conditions (6), which determine c_1 and c_2. This semi-analytical formula reproduces all actions within an average error of 0.1%. Finally, one can approximate the remaining difference by a convenient fit-function which preserves the correct boundary conditions as $\alpha \to 0$ and $\alpha \to \alpha_{PO}$. We find that with the choice

$$J(a) = J_M + c_1 a + c_2 a^2 + J_{\text{diff}}(a) \tag{10}$$

where

$$J_{\text{diff}}(a) = \sum_{n=3}^{n_{\max}} d_n a^{n/3} (a - a_{PO})^2, \tag{11}$$

it is sufficient to incorporate the first three terms with adjusted coefficients d_i to reproduce all the data within an error of less than 10^{-6}. The corresponding function $J(\alpha)$ is drawn as a solid line in Fig. 2.

According to Eq. (4) and $dJ/d\alpha = J_1$, the action functional can now be used to calculate the individual actions J_1 and J_2, and to plot the energy shell in the J_1/J_2 plane, which is done in Fig. 3. Note that as $J_1 \to 0$, J_2 tends to S_{PO} whereas J_1 becomes singular as J_2 approaches $\sqrt{2}$. The singularity reflects the fact that the outer electron approaches a (single-particle) ionization threshold with diverging accumulated action indicating the existence of infinitely many quantized bound (Rydberg) states below that threshold.

III. TORUS QUANTIZATION

With the energy-surface at hand, it is straightforward to quantize the action integrals separately. We emphasize that the torus quanti-

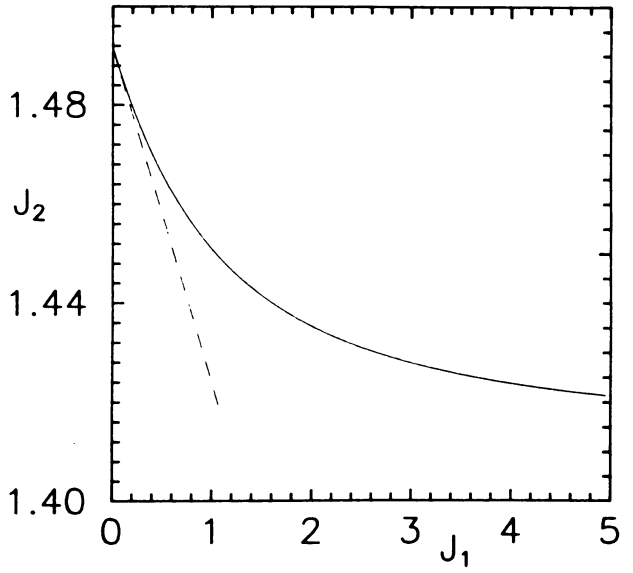

FIGURE 3 Energy surface $E = -1$ in the J_1/J_2-action plane for the collinear configuration with both electrons on the same side of the atom ($Z = 2$). The Gutzwiller periodic orbit approximation is drawn as a dashed line.

zation for the monopole Hamiltonian (7), (8) with $J_1 = n + 1, J_2 = l + 1$ gives the *exact* monopole bound state spectrum

$$E_{nl} = -\frac{Z^2}{2(n+1)^2} - \frac{(Z-1)^2}{2(l+1)^2}. \tag{12}$$

This result merely reflects the exactness of the torus quantization procedure for the hydrogen atom (the monopole Hamiltonian describes nothing but two decoupled hydrogen atoms having different Rydberg constants). However, even for the hydrogen atom it is not well established that semiclassical torus quantization gives the exact energies.[18]

Eigenenergies of the full (three-dimensional) problem are determined by an action functional similar to Eq. (4),

$$J(\alpha_1, \alpha_3) = J_2 + \alpha_1 J_1 + 2\alpha_3 J_3 \tag{13}$$

where α_1, α_3 are the winding numbers of the tori with quantized actions $J_2 = n + \mu_2$, $J_1 = l + \mu_1$, and $J_3 = k + \mu_3$. For the full three-dimensional problem the bending degree locally described by J_3 appears twice, once for bending motion within the body fixed plane spanned by the three particles, and once for the bending motion perpendicular to the plane, both of which are equivalent. The μ_i are appropriate Maslov indices, $\mu_i = 1/2$ in this case. The Gutzwiller approximation (2) consists of replacing the action functional and the winding numbers by their values at the periodic orbit. This describes the energy shell correctly to first order near the PO, $J_2 = S_{PO}/\sqrt{-E} - \alpha_1^{PO} J_1 - \alpha_3^{PO} J_3$ as demonstrated in Fig. 3 for $J_3 = 0$. Obviously, we can expect the Gutzwiller approximation to be of good quality only for $J_2 \gg J_1, J_3$.

For the energetically highest Rydberg series converging to the N-threshold of the He^+ ion, we have, associated with the action variables (J_2, J_1, J_3), the set of quantum numbers $(n, l, k) = (N-1, l, 0)$ with l ranging from 0 to ∞. For $k = 0$ we may approximate the third degree of freedom by a Gutzwiller-type replacement, i.e., we linearize the bending degree of freedom in the neighborhood of $J_3 = 0$. This gives a smooth approximation of α_3 as a function of α_1 with $\alpha_3(\alpha_1^{PO}) = \alpha_3^{PO}$ and $\alpha_3(0) = 1/2$. The last property ensures the correct threshold energies as $l \to \infty$.

The energies so obtained are compared in Table I with the (numerically) exact quantum results obtained by large scale calculations[19] for $N = 5, 8, 16$. Obviously, the states form Rydberg series converging to the various N-thresholds. Not only does the absolute error of the EBK-quantization quickly tend to zero, but also the quantum defects become exact as $n \to \infty$. This can be seen in column 5 of Table I where the relative error ε_{EBK} with respect to the *single*-particle threshold $E_N = Z^2/2N^2$ is given, i.e.,

$$\varepsilon_{EBK} = \left| \frac{E_{EBK} - E_{QM}}{E_N - E_{QM}} \right| . \tag{14}$$

Asymptotically the error values decrease proportional to $(\mu_{QM}^{\infty} - \mu_{EBK}^{\infty})/l$, where μ^{∞} are the asymptotic ($l \to \infty$) quantum defects. We

TABLE I

Energies for various double-Rydberg states of frozen planet type (with $k = 0$). The quantum energies E_{QM} are taken from a highly accurate compilation of helium states below the $N = 10$ threshold (Ref. 19); the semiclassical energies E_{EBK} are obtained by quantizing the various action integrals; the energies E_{qex} obtained by a quadrupole expansion of the electron–electron interaction are calculated using Table I of Ref. 10.

n	l	E_{QM}	E_{EBK}	ε_{EBK}	E_{qex}	ε_{qex}
4	0	0.089570804	0.0890186	5.8	0.08814	15.0
4	1	0.087559623	0.0870293	7.0	0.08640	15.4
4	2	0.086097676	0.0856363	7.6	0.08516	15.3
4	3	0.085006172	0.0846186	7.7	0.08426	15.0
4	4	0.084170732	0.0838520	7.6	0.08357	14.5
4	5	0.083520956	0.0832604	7.4	0.08303	13.9
4	6	0.083008587	0.0827946	7.1	0.08261	13.2
4	7	0.082597947	0.0824215	6.8	0.08227	12.6
4	8	0.082264628	0.0821181	6.5	0.08199	12.0
4	9	0.081990801	0.0818681	6.2	0.08176	11.4
4	∞	0.08	0.08		0.08	
7	0	0.034842643	0.0347777	1.8	0.03435	13.9
7	1	0.034312420	0.0342541	1.9	0.03391	13.1
7	2	0.033890165	0.0338406	1.9	0.03356	12.5
7	3	0.033548909	0.0335072	1.8	0.03328	11.9
7	4	0.033268260	0.0332342	1.7	0.03304	11.3
7	5	0.033035777	0.0330077	1.6	0.03284	10.7
7	6	0.032841466	0.0328177	1.5	0.03267	10.3
7	7	0.032675343	0.0326568	1.3	0.03254	9.7
7	8	0.032532950	0.0325194	1.1	0.03242	9.1
7	∞	0.03125	0.03125		0.03125	
15	0	0.008697058	0.00869328	0.4		
15	1	0.008627712	0.00862373	0.5		
15	2	0.008566204	0.00856224	0.5		
15	∞	0.0078125	0.0078125			

remark that the quantum defects (and also the renormalized widths $\Gamma_l l^3$) of the quantum calculations converge only slowly against their asymptotic values.[19]

In Refs. 9 and 10 an independent-electron type Rydberg formula

$$E_{n_2 n_r \gamma} = -\frac{Z^2}{2n_2^2} - \frac{(Z-1)^2}{2(n_r + l^{\gamma}_{\text{eff}} + 1)^2} \tag{15}$$

derived from a multipole expansion of the electron–electron interaction was proposed as a simpler and more transparent description of the FPC. The quantum numbers are to be identified as $(n, l, k) \equiv (n_2, n_r, \gamma)$. We already argued in Ref. 5 that even though the multipole expansion asymptotically describes the effective potential for the outer electron, the quantitative (and even partly the qualitative) picture is poor, particularly in describing the character of the lowest state of each Rydberg series. In Table I we give the predictions of Eq. (15) together with the errors ε_{qex}, for which the leading dipole term l_{eff} is already corrected by the next term in the multipole expansion. As can be seen the error is much larger than for the semiclassical torus quantization and it does not seem to become significantly smaller for higher n. In fact, whereas the semiclassical formulas (2), (13) become better and better for high n (even *exact* for $n \to \infty$[5]) the dipole formula (15) has an asymptotic *absolute* error of ~4% for the first state of each Rydberg series (this can be deduced from the values of Table I given in Ref. 9, implying a diverging error for the energies *relative* to the corresponding single-particle escape threshold. Thus, apart from the poor description of the low lying states, the dipole formula completely fails in predicting asymptotically ($n \to \infty$) the FPC series.

IV. SUMMARY AND CONCLUSION

To conclude, we have shown explicitly that the Gutzwiller approximation (2) is the correct limit of the semiclassical torus (EBK) quantization for the FPCs. We have shown this for $L = 0$, but the theory can be extended straightforwardly to $L \neq 0$. The Gutzwiller approximation applies whenever the nodal excitation n along the fundamental PO is large compared to transverse excitations k, l. However, a full torus quantization procedure has to be applied for calculating the Rydberg series for fixed n and $l \to \infty$. To a large extent this can be done analytically, and only a couple of trajectories have to be run to determine the energy shell in action variables to high accuracy. The quantized energies (and thresholds) thus obtained are exact in the limit $l \to \infty$, but the error in the asymptotic quantum defect remains finite for finite n. However, even this error

vanishes in the semiclassical limit $n \to \infty$ independent of the value of l. The semiclassical formalism does not require all quantum numbers to be large, i.e., even the quantization of the zero point motion for $k = 0$ and/or $l = 0$ becomes exact in this limit. In contrast, a low-order multipole expansion completely fails in predicting the energies asymptotically ($n \to \infty$). Even though a multipole expansion may describe the potential for the outer electron sufficiently well for large distances, the electron correlation at short and intermediate distances is not well enough described within the model.

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