On the $3n + l$ Quantum Number in the Cluster Problem

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I. INTRODUCTION

The electronic shell structure observed in mass spectra of metal clusters can be rather well described by an independent electron model. Treating the valence electrons of the cluster as an ideal Fermi gas moving in an external potential $V(\vec{r})$, a shell structure arises from the discreteness of energy levels for particles confined to a finite volume. This approach forms the basis for the semi-classical description of the electronic shell and supershell structure. Suitable model potentials can be obtained from self-consistent density functional calculations. It can be verified that the electronic shell structure may be determined from the spectrum of a one-particle Hamiltonian, provided the $V(\vec{r})$ is chosen sufficiently close to the self-consistent potential.

For small sodium clusters of 8 up to 92 atoms it has been shown that the shell structure arises from successively filling the $2(2l + 1)$-fold degenerate energy levels $\epsilon_{n,l}$ of a spherically symmetric potential. To uniquely characterize the energy levels for such potentials we use the number $n$ of nodes in the radial wave function, while $l$ denotes the angular momentum quantum number. Going to larger clusters reduces the influence of a single energy level on the shell structure. Nevertheless even for clusters of several thousand atoms electronic shell structure has been observed. This suggests that the energy levels bunch together in groups of (nearly) constant energy. Actually, the experimental results for sodium clusters of up to approximately 1500 atoms indicate that these bunches may be formed by degenerate energy levels $\epsilon_{n,l}$ corresponding to definite values of $3n + l$. It has been pointed out that quantities of the type $an + \beta l$ characterize two exactly solvable quantum mechanical problems: the hydrogen atom, in which levels with the same $n + l$ are degenerate, and the isotropic harmonic oscillator, where the degeneracy is described by the quantum number $2n + l$. With this analogy in mind it has been conjectured that there might be a set of solutions of the radial Schrödinger equation displaying the degeneracy described by the quantum number $3n + l$.

At first sight a theorem from classical mechanics seems to imply that there is no such radial potential. The theorem states that only for central potentials of the form $-1/r$ and $r^2$ all bounded orbits are closed. Assuming that this property is caused by a dynamical symmetry of the system which uniquely corresponds to a symmetry of the quantized system, this would imply that only these two problems exhibit “accidental” degeneracies. Unfortunately the situation is not that simple. While it is known that the degeneracies for the quantum mechanical Kepler problem and the harmonic oscillator are a consequence of the dynamical symmetries $so(4)$ and $su(3)$, respectively, it turns out that all classical systems involving 3 degrees of freedom automatically possess both $so(4)$ and $su(3)$ symmetry. To our knowledge, the question whether the hydrogen atom and the harmonic oscillator are the only radially symmetric quantum mechanical systems possessing a dynamical symmetry has not been settled so far. A discussion of near degeneracies of the type $an + \beta l$ in the context of semiclassical quantization has been given by Bohr and Mottelson.

Besides being interesting in its own right, identifying an exactly solvable problem possessing a quantum number $3n + l$ would be important for two reasons. First, it would provide us with the optimal basis set for self-consistent computations of the total energy of metal clusters. Second, it would give the ideal starting point for treating realistic cluster potentials by perturbation theory.

In the present paper, we investigate whether the number $3n + l$ is analogous to the quantum numbers $n + l$ and $2n + l$. First we argue that a degeneracy described by the quantum number $3n + l$ cannot be caused by a dynamical symmetry related to a classical Lie algebra. Next we show that in three dimensions there are exactly two potentials fulfilling the shape-invariance condition of supersymmetric quantum mechanics for spherically symmetric problems, namely the Coulomb potential and the harmonic oscillator. Finally we numerically optimize radial potentials to exhibit the $3n + l$-degeneracy. We find, within the limits of our calculations, that there is no exactly solvable ‘cluster potential’ with $3n + l$-degeneracy. We therefore conclude that $3n + l$ is not a proper quantum number as $n + l$ and $2n + l$ are.
II. CLASSICAL SYMMETRY

A quantum mechanical system is said to exhibit a symmetry if its Hamiltonian is invariant with respect to the operations of some Lie algebra. A well-known example is spherical symmetry: the Hamiltonian \( H \) of a radially symmetric system commutes with the angular momentum operators:

\[
[L_i, H] = 0.
\]  

Since \( \{L_x, L_y, L_z\} \) forms a Lie algebra, namely the angular momentum algebra \( su(2) \), the Hamiltonian is said to be invariant under \( su(2) \). As an immediate consequence of \( su(2) \) the eigenspaces \( \mathcal{H}_{\epsilon_{n,1}} \) of the Hamiltonian are invariant under the action of the \( L_i \), i.e. they are representation spaces of the symmetry algebra. For a generic radial potential, the \( \mathcal{H}_{\epsilon_{n,1}} \) will be irreducible representation spaces of the angular momentum algebra. For these systems \( su(2) \) is the full symmetry.

There are, however, special cases in which the eigenspaces of the Hamiltonian are reducible. Examples are the hydrogen atom and the isotropic harmonic oscillator. For the former, energy levels \( \epsilon_{n,l} \) having the quantum number \( n + l \) in common are degenerate, for the latter the respective quantum number is \( 2n + l \). It is well known that these degeneracies are not accidental, rather they are the consequence of a symmetry higher than spherical. For the hydrogen atom this symmetry is described by the algebra \( so(4) \) while for the harmonic oscillator the symmetry algebra is the \( su(3) \).

Having identified \( 3n + l \) as a candidate for a new quantum number, the question arises as to whether the corresponding degeneracy is also due to some hidden symmetry.

To answer this question, we exploit the fact that eigenspaces of a Hamiltonian are representation spaces of its symmetry algebra. In particular, the dimensions of these spaces must coincide. Fortunately, representation theory provides us with all the information needed. The irreducible representations of the classical Lie algebras \( \{su(k + 1), so(2k + 1), sp(2k), so(2k)\} \), corresponding to the algebras \( A_k, B_k, C_k, \) and \( D_k \) in the complete classification scheme of all semisimple Lie algebras) can be labeled using the Cartan subalgebra. For a Lie algebra of rank \( k \) this is a set of \( k \) commuting operators. They can be chosen such that they have integer eigenvalues. For any given representation one can find a basis which diagonalizes the operators in the Cartan subalgebra. Each basis vector is then characterized by the corresponding integer vector of eigenvalues \( \{m_1, \ldots, m_k\} \), its ‘weight’. Furthermore each irreducible representation is uniquely determined by the highest weight of its basis vectors according to lexicographical ordering. The dimension of the irreducible representation with highest weight \( \{n_1, \ldots, n_k\} \) is given by Weyl’s dimensionality formula

\[
\dim(\Gamma_{\mathcal{L}}(n_1, \ldots, n_k)) = \prod_{\alpha \in \Delta_+} \left( \frac{\sum_{j=1}^{k} c_j^{(\alpha)} n_j + 1}{\prod_{j=1}^{k} c_j^{(\alpha)}} \right).
\]  

The constants \( c_j^{(\alpha)} \) and the set \( \Delta_+ \) of positive roots only depend on the type of the Lie algebra, not on any particular representation. Hence for a given classical Lie algebra, the dimensions of the irreducible representations are given by a polynomial in the highest weights. As an example we write down explicit expressions for the dimensions of the classical algebras of rank two:

\[
\dim(\Gamma_{A_2}(n_1, n_2)) = \frac{(n_1 + 1)(n_1 + n_2 + 2)(n_2 + 1)}{2},
\]
\[
\dim(\Gamma_{B_2}(n_1, n_2)) = \frac{(n_1 + 1)(n_1 + n_2 + 2)(2n_1 + n_2 + 3)(n_2 + 1)}{6},
\]
\[
\dim(\Gamma_{D_2}(n_1, n_2)) = (n_1 + 1)(n_2 + 1).
\]

These have to match the dimensions of the eigenspaces of the Hamiltonian. Given the quantum number \( N \) associated with the degeneracy of energy levels \( \epsilon_{n,l} \), the orders \( g_{N_k} \) of the degeneracies can be readily computed. For the quantum number \( N_1 = n + l \) we obtain

\[
g_{N_1} = (N_1 + 1)^2;
\]
\[
N_2 = 2n + l \quad \text{leads to} \quad g_{N_2} = \frac{(N_2 + 1)(N_2 + 2)}{2},
\]
and \( N_3 = 3n + l \) to

\[
g_{N_3} = \begin{cases} \frac{1}{2}(N_3 + 2)^2, & \text{for } N_3 \equiv 1 \pmod{3}, \\ \frac{1}{2}(N_3 + 1)(N_3 + 3), & \text{otherwise.} \end{cases}
\]

Through comparing with expressions \( \eqref{eq:dimB2} \)-\( \eqref{eq:dimD2} \), we find

\[
g_{N_1} = \dim(\Gamma_{D_2}(N_1, N_1)),
\]
\[
g_{N_2} = \dim(\Gamma_{A_2}(N_2, 0)),
\]
indicating that the eigenspaces of the Hamiltonian for the hydrogen atom might be irreducible representation.
spaces of the Lie algebra $D_4 \equiv so(4)$ with highest weights $(n_1, n_2) = (N_1, N_1)$ — as indeed it is. Similarly for
the harmonic oscillator the eigenspaces could be the irre-
ducible representation spaces of $A_2 \equiv su(3)$ with highest
weights $(n_1, n_2) = (N_2, 0)$ — again, as indeed it is. For
the quantum number $3n + l$ the situation is fundam-
ently different. The degeneracies of the eigenspaces are no
longer given by a closed formula, i.e. there is no simple
relation between the quantum number and the highest
weights of some Lie algebra. If there existed a quantum
mechanical operator corresponding to the quantum num-
er, which would be a Casimir operator of the symmetry
mechanical operator corresponding to the quantum num-
er. Thus, we cannot
find a classical Lie algebra that could cause a degeneracy
corresponding to the quantum number $3n + l$. The same
reasoning holds for quantum numbers $\alpha n + l$ with $\alpha > 3$.

III. SUPERSYMMETRY

An elegant approach to exactly solvable problems is
provided by supersymmetric quantum mechanics. The
basic idea of the method is that a given Hamil-
тонian

$$H^- = -\frac{d^2}{dx^2} + V^-(x)$$

(11)
can be factorized if the energy of the ground state $\Psi_0(x)$ is
set to zero:

$$H^- = Q^+Q^-,$$ where $Q^\pm \equiv \left(\pm \frac{d}{dx} - \frac{\Psi_0^*}{\Psi_0}\right)$.

(12)

Here the prime denotes the derivative with respect to $x$. Reversing the order in the factorization, a new Hamiltonian

$H^+ \equiv Q^-Q^+$

can be defined. It is called the supersymmetric partner of $H^-$. Obviously the $Q^\pm$ intertwine the Hamiltonians:

$$H^-Q^+ = Q^+H^-,$$

(13)

$$H^+Q^- = Q^-H^+.$$ (14)

Thus, except for the ground state of $H^-$, which is anni-
hilated by $Q^-$, the spectra of the Hamiltonians $H^\pm$ are
identical. This situation is illustrated in Fig. 1.

The potentials corresponding to the Hamiltonians $H^\pm$
can be derived from the superpotential

$$W(x) \equiv -\frac{\Psi_0^*}{\Psi_0}$$

(15)

via

$$V^\pm(x) = \left(W(x)^2 \mp W'(x)\right).$$

(16)

For a generic Hamiltonian the potential $V^-(x)$ and its
supersymmetric partner $V^+(x)$ will be of different shape.

$$H^- = Q^+Q^- \quad H^+ = Q^-Q^+$$

\[
\begin{array}{c}
\vdots \\
Q^+ \\
E^-_1 & \rightarrow & E^+_1 \\
Q^- & \rightarrow & E^-_0 \\
\end{array}
\]

**FIG. 1.** Spectra of supersymmetric partner Hamiltonians $H^-$ and $H^+$ (non broken supersymmetry).

If, however, they only differ in some parameters and a
constant offset, i.e. if

$$V^+(a_0; x) = V^-(a_1, x) + R(a_0),$$

(17)

the corresponding Hamiltonian is exactly solvable. In
what follows we shall refer to the expression in equation (17) as the shape-invariance condition. In such a case,

$$V^-(a_k; x) ^{SU3} V^+(a_k; x) = V^-(a_{k+1}; x) + R(a_k)$$

(18)

of supersymmetric partner potentials can be constructed.

From the knowledge of the ground-state energy in the
potential $V^-(a_1; x)$ as a function of the parameters $a$, the
whole spectrum of the initial Hamiltonian $H^-$ can be
obtained:

$$E_n^- = \sum_{k=0}^{n-1} R(a_k).$$

(19)

We now investigate whether a radial problem with de-
gen eracies according to the quantum number $3n + l$ can
be constructed using the above ideas. More specifically,
we are looking for any potential $U(r)$ such that energy
levels with different angular momentum $l$ are degenerate.

For the radial potentials

$$V(l; r) \equiv U(r) + \frac{l(l+1)}{r^2}$$

(20)

the shape-invariance condition (17) reads

$$V^+(l; r) = V^-(l; r) + R(l).$$

(21)

Using (20) this can be rewritten as

$$V^+(l; r) = V^-(l; r) + \frac{2\lambda_l}{r^2} + 2\beta_l,$$

(22)

where we have introduced the notations

$$2\lambda_l = l(l+1) - \tilde{l}(\tilde{l}+1) \quad \text{and} \quad 2\beta_l = R(l).$$

(23)
Inserting (14) into (22), we obtain a differential equation for the superpotential $W(l; r)$, the general solution of which is

$$W(l; r) = -\frac{\lambda_i}{r} + \alpha_l + \beta_l r. \quad (24)$$

The corresponding potentials are

$$V^\pm(l; r) = \frac{\lambda_i(\lambda_i \pm 1)}{r^2} - \frac{2\lambda_i \alpha_l}{r} - (2\lambda_i \pm 1)\beta_l + (\alpha_l + \beta_l r)^2. \quad (25)$$

The choices $\lambda_i = l + 1$ and $\lambda_i = -l$ will make $V^-(l; r)$ a radial potential with angular momentum $l$. To ensure that we can normalize the ground state, the parameters in the above equations must satisfy

$$\lambda_i > -\frac{1}{2}, \quad \text{and} \quad \left\{ \begin{array}{l} \beta_l > 0, \\
\beta_l = 0, \quad \alpha_l > 0. \end{array} \right. \quad (26)$$

We thus have to choose $\lambda_i = l + 1 > -1/2$. Inserting this into equation (25) yields

$$V^+(l; r) - V^-(l + 1, r) = \left\{ \begin{array}{l} (\alpha_l + \beta_l r)^2 - (\alpha_{l+1} + \beta_{l+1} r)^2 \\
- \frac{2(l + 1)\alpha_l}{r} - \frac{2(l + 2)\alpha_{l+1}}{r} \\
+ \left\{ - (2l + 1)\beta_l + (2l + 5)\beta_{l+1} \right\}. \end{array} \right. \quad (27)$$

To be consistent with (17), we require the right-hand side of the above equation to be constant. By comparing the coefficients, we find exactly two solutions of the shape-invariance condition:

$$\frac{\alpha_{l+1}}{\alpha_l} = \frac{l + 1}{l + 2} \quad \text{and} \quad \beta_l = 0, \quad (28)$$

or

$$\alpha_l = 0 \quad \text{and} \quad \beta_l = \text{const.} \quad (29)$$

The first solution corresponds to the Hamiltonian for the hydrogen atom. Setting $\alpha_l = q/(2(l + 1))$ we obtain the energy spectrum

$$\epsilon_{n,l} = E(l)^n_n = -\frac{q^2}{4(n + l + 1)^2} \quad (30)$$

pertaining to the Coulomb potential $V(r) = -q/r$. Writing the constant in the second solution as $\beta_l = \omega/2$ we find the spectrum of the harmonic oscillator $V(r) = \omega^2 r^2/4$:

$$\epsilon_{n,l} = E(l)^n_n = (2n + l + 3/2)\omega. \quad (31)$$

Obviously, the spectra of these systems are characterized by degeneracies according to the quantum numbers $n + l$ and $2n + l$. Thus we have shown that there exist exactly two physically acceptable radial potentials which fulfill the shape-invariance condition (21), namely those associated with the quantum numbers $n + l$ and $2n + l$. It thus appears that these two quantum numbers are unique.

**IV. NUMERICAL OPTIMIZATION**

Clearly, arguments of the type given above can only exclude the existence of a system with quantum number $3n + l$ under the assumption of some specific mechanism (e.g., classical symmetry or supersymmetry) that would cause the degeneracy. Thus, by such reasoning it is not possible to give a general proof that such a system cannot exist. Furthermore, it is conceivable that $3n + l$ is only an approximate quantum number, i.e. that levels of quantum number $3n + l$ are not exactly but merely near-degenerate. Therefore, we will now approach the problem at hand from a completely different direction.

We try to construct cluster-potentials exhibiting degeneracies according to $3n + l$ by numerical optimization. The basic idea is to transform the continuous eigenvalue problem for the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \Delta + V(r) \quad (32)$$

into a finite dimensional problem by discretizing the Schrödinger equation. Discretizing the potential

$$\left\{ V(r) \mid r \in [0, \infty) \right\} \mapsto \left\{ V_i \mid V_i = V(r_i) \right\}, \quad (33)$$

the eigengenvalues can be considered as functions of a finite number of potential parameters $V_i$ instead of being functionals of the potential:

$$\epsilon_{n,l}[V(r)] \approx \epsilon_{n,l}(\{V_i\}). \quad (34)$$

A potential with the postulated $3n + l$ degeneracy can then be found by numerically optimizing a suitable initial potential with respect to a cost function, which measures the deviation from the desired degeneracy. By a straightforward application of the above strategy we have found that the $V_i$’s for successive $i$’s oscillate wildly. For such potentials $\{V_i\}$ the approximation (34) is clearly invalid. Thus we have imposed a constraint on the $V_i$’s to keep the potential smooth. Furthermore we have made sure that the number of electrons the potential can hold for a given Fermi energy does not vary too much.

We have performed such optimizations starting from Woods-Saxon potentials

$$V(r) = \frac{-V_0}{1 + \exp\left(\frac{r - R_0}{a}\right)} \quad (35)$$

with sodium-like parameters ($V_0 = 0.46 \text{Ry}$ and $a = 0.94 a_0$) for varying cluster sizes $R_0$. For the discretization we have used a mesh of step width $\Delta r \approx r_\ast/40$. 


FIG. 2. Result of an optimization run for the quantum number $2n + l$. The optimized potential (full line) along with the energy levels (horizontal lines) are plotted. The computation was started from a Woods-Saxon potential of width $R_0 = 8 r_s$, with $r_s = 3.93 a_0$ (dotted line). The quadratic potential (dashed-dotted line) exhibiting the exact $2n + l$-degeneracy is given for comparison.

A cost function has measured the non-degeneracy of the energy levels, the smoothness of the potential and the variation in the number of electrons that fit into the potential for a given Fermi energy. To find the non-degeneracy we have determined for each quantum number $N_3 = 3n + l$ the average energy

$$\bar{\epsilon}_{N_3} = \frac{\sum_{3n+l=N_3} 2(2l+1) \epsilon_{n,l}}{\sum_{3n+l=N_3} 2(2l+1)}.$$  \hspace{1cm} (36)

The deviation of the eigenstates from the desired degeneracy was then defined as

$$\sum_{N_3} \sum_{3n+l=N_3} 2(2l+1) \frac{(\epsilon_{n,l} - \bar{\epsilon}_{N_3})^2}{\sum_{3n+l=N_3} 2(2l+1)}.$$ \hspace{1cm} (37)

As a measure of the roughness of the potential represented by the $V_i$ we have used the expression

$$\sum_i (V_{i-1} - 2V_i + V_{i+1})^2,$$ \hspace{1cm} (38)

which disfavors sharp bends in $V(r)$. The number of electrons fitting into the potential was estimated by the Thomas-Fermi expression

$$N_{el} = \frac{4}{3\pi} \int_0^{r_{out}} dr \ r^2 \left( \frac{2m}{\hbar^2} \left( E_F - V(r) \right) \right)^{3/2},$$ \hspace{1cm} (39)

where $r_{out}$ is the classical turning point for the potential $V(r)$.

Since the Woods-Saxon potential has only a finite number of bound states, the summation (37) has to end at some maximal $N$, which we will denote by $N_{max}$.

To demonstrate that with the above measures we indeed can find potentials with a given degeneracy, we have

FIG. 3. Potentials for increasing cluster radius $R_0$, optimized for degeneracies according to the quantum number $3n + l$. The optimization was started from Woods-Saxon potentials with sodium-like parameters. $r_s = 3.93 a_0$ is the Wigner-Seitz radius of Na. The lines indicate the position of the energy levels.
tested our program on the quantum number $2n + l$. We start from the sodium-like Woods-Saxon potential that we also use for the $3n + l$-optimizations. Although this initial potential is much closer to a $3n + l$ than to a $2n + l$-degeneracy, it turns out that during optimization the energy levels are very easily arranged into equidistant shells. For all choices of $N_{\text{max}}$ nearly perfect degeneracy is achieved for the shells with $N < N_{\text{max}}$. Interestingly, even the levels which are excluded from the cost function (i.e. those above $N_{\text{max}}$) tend to form degenerate shells. Figure 2 shows the energy spectrum along with the potential resulting from the optimization of a Woods-Saxon potential with $R_0 = 8 r_s$. As can be seen the optimized potential approximates well the quadratic potential (indicated by the dash-dotted line) associated with the $2n + l$ degeneracy, although it is very different from the initial potential (dotted line).\[8\]

To make the results for different cluster sizes comparable, we have chosen $N_{\text{max}}$ to correspond always to the shell closest to Fermi energy. It turns out that for small clusters the energy levels can be forced to form nearly degenerate shells according to the quantum number $3n + l$. The corresponding potentials, however, exhibit large oscillations inside the cluster. These seem to be fairly unrealistic, when compared to those obtained form self-consistent calculations.\[8\] For larger clusters the situation becomes even worse. Here, although the optimized potentials oscillate strongly, degeneracy can merely be achieved for the states with $3n + l$ just below $N_{\text{max}}$. In other words, only just below $E_F$ a grouping of almost degenerate energy levels can be observed. Above and further below $N_{\text{max}}$ there are no large gaps in the spectrum, and hence no shells.

The above results suggest that the outcome of a degeneracy optimization strongly depends on $N_{\text{max}}$, indicating that there is no unique ‘cluster potential’ which

FIG. 4. Optimization of cluster potentials for degeneracies according to the quantum number $3n + l$. On the left, potentials are plotted along with the energy levels. The grouping of levels is shown on the right, where the eigenenergies $\epsilon_{n,l}$ are plotted over the corresponding angular momenta $l$. Levels having the same quantum number $3n + l$ are connected by a dotted line. The plots at the top show the spectrum of the Woods-Saxon potential, which has been used as initial potential for the optimization runs shown in the plots below. These runs only differ in the number $N_{\text{max}}$ of shells included in the cost function.
could be approximated by the optimized potentials. To demonstrate this dependence, we have performed calculations with different values of \( N_{\text{max}} \) for a fixed cluster size. The results are shown in Fig. 4. At the top the Woods-Saxon potential, which was used as starting point in the optimization runs, along with its energy spectrum is plotted. On the left-hand side the potential is shown as in Fig. 3 (except that we restrict the energy axis to a smaller range). To the right the eigenstates \( \epsilon_{n,l} \) are arranged according to their angular momenta \( l \). States belonging to the same shell \( N_3 = 3n + l \) are connected by a dotted curve. A shell \( N_3 \) is (near-)degenerate if this curve is a horizontal line. The greater its slope, the worse the degeneracy. Optimizing the potential for two different values of \( N_{\text{max}} \) results in the potentials shown in the lower part of Fig. 4. These potentials are markedly different. Not only the amplitude of the oscillations, even the number of maxima in \( V(r) \) changes with \( N_{\text{max}} \). As can be seen from the spectra on the right-hand side the dotted curves connecting states, which belong to the same shell \( N_3 = 3n + l \) are concave for \( N_3 > N_{\text{max}} \) and convex for \( N_3 < N_{\text{max}} \). Comparing the spectra for \( N_{\text{max}} = 10 \) and 12, we observe that there is a tradeoff between straightening out the dotted lines above \( N_3 = 10 \) and bending those corresponding to smaller quantum numbers; i.e. it seems to be impossible to obtain the desired degeneracy for \( ad \) shells. Furthermore it turns out that the higher \( N_{\text{max}} \) (i.e. the more states are included in the cost function), the stronger are the oscillations in \( V(r) \).

If a ‘cluster potential’ having a shape similar to a Woods-Saxon potential existed, then the optimized potentials would have approximated that unique potential. Like in the optimizations for the quantum number \( 2n + l \), the degeneracies would become the better the larger \( N_{\text{max}} \). This is clearly not what we have found in our calculations. Instead, the optimized potentials strongly depend on \( N_{\text{max}} \) and further we have not found any potential whose complete spectrum is degenerate according to the quantum number \( 3n + l \).

V. CONCLUSIONS

By use of analytic methods as well as numerical calculations we have argued that there is no ‘cluster problem’ analogous to the exactly solvable problems of the hydrogen atom and the harmonic oscillator. The sequence of quantum numbers \( n + l \) and \( 2n + l \) characterizing the latter systems thus cannot be simply extended to quantum numbers \( 3n + l \). In this sense it seems that the quantum numbers \( n + l \) and \( 2n + l \) are unique.

In spite of this, the higher ‘quantum numbers’ \( \alpha n + \beta l \) do have some meaning. The analysis of the energy levels near the Fermi energy found in self-consistent jellium calculations reveals that the electronic shell and super-shell structure mainly arises from an interplay of near degeneracies of the type \( 3n + l \) and \( 4n + l \). As has been pointed out by Bohr and Mottelson, such near degeneracies of energy levels corresponding to numbers \( \alpha n + \beta l \) are related to classical periodic orbits. For example, triangular orbits are connected with \( 3n + l \)-degeneracies, and square orbits with \( 4n + l \). This simple correspondence is however lost in a full semiclassical analysis. Nevertheless for typical cluster potentials a periodic orbit expansion shows that the electronic shell and supershell structure is essentially captured by only considering the most important contributions which stem from the triangular and the square orbits. Using the simple picture of Bohr and Mottelson this is consistent with the conjectured degeneracies as well as with those that can be found in jellium calculations.

Thus, the structures observed in the mass spectra of warmed metal clusters are intimately related with the quantities \( 3n + l \) and \( 4n + l \). These numbers are, however, not analogous to the quantum numbers known from the exactly solvable models.

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29 A detailed analysis of how the Kohn-Sham orbitals are populated in self-consistent jellium calculations will be published elsewhere.