Unitary group approach for effective potentials in 3D systems

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3D harmonic oscillator

\[ \hat{H}_{cs} = \frac{1}{2m} \mathbf{p}^2 + \frac{m\omega^2}{2} \mathbf{q}^2. \]  

(1)

The corresponding eigenfunctions are

\[ \Psi_{nlm}(q, \theta, \phi) = A_{nl} q^l e^{-q^2/2} L_{(n-l)/2}^{l+1/2}(q^2) Y_m(\theta, \phi). \]  

(2)
The Hamiltonian takes the form
\[ \hat{H}_{\text{h.o.}} = \hbar \omega (\hat{n} + 3/2) \]
with \( \hat{n} = \sqrt{3} [a^\dagger \times \tilde{a}]_0^{(0)} \), and eigenfunctions
\[ |nlm\rangle = B_{nl} (a^\dagger \cdot \hat{a}^\dagger)^{(n-l)/2} \mathcal{Y}_m^{l}(\hat{a}^\dagger)|0\rangle \]
where
\[ \mathcal{Y}_m^{l}(\hat{a}^\dagger) = 2^{-l/2} (\hat{a}^\dagger \cdot \hat{a}^\dagger)^{l/2} Y_m^l(\hat{a}^\dagger). \]

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Addition of a scalar boson $s^\dagger(s)$.

Bilinear products are generators of the $U(4)$ group

$$\hat{n}_a = \sqrt{3}[a^\dagger \times \tilde{a}]_0^{(0)}; \quad \hat{n}_s = s^\dagger s,$$

$$\hat{L}_\mu = \sqrt{2}[a^\dagger \times \tilde{a}]_\mu^{(1)}; \quad \hat{D}_\mu = a^\dagger_\mu s - s^\dagger \tilde{a}_\mu,$$

$$\hat{Q}_\mu = [a^\dagger \times \tilde{a}]_\mu^{(2)}; \quad \hat{R}_\mu = i(a^\dagger_\mu s + s^\dagger \tilde{a}_\mu).$$

The algebra $U(4)$ provides the following three chains

$$U(4) \supset U(3) \supset SO(3) \supset SO(2),$$

$$U(4) \supset SO(4) \supset SO(3) \supset SO(2),$$

$$U(4) \supset \overline{SO}(4) \supset SO(3) \supset SO(2),$$

with the following generators

$$G_{U(3)} = \{\hat{n}_a, \hat{L}_\mu, \hat{Q}_\mu\},$$

$$G_{SO(4)} = \{\hat{D}_\mu, \hat{L}_\mu\},$$

$$G_{\overline{SO}(4)} = \{\hat{R}_\mu, \hat{L}_\mu\}.$$
The CSCO associated with this chain establishes the basis

\[ \hat{N} |[N]_{n_a LM}\rangle = N |[N]_{n_a LM}\rangle \]

\[ \hat{n}_a |[N]_{n_a LM}\rangle = n_a |[N]_{n_a LM}\rangle \]

\[ \hat{L}^2 |[N]_{n_a LM}\rangle = L(L+1) |[N]_{n_a LM}\rangle \]

\[ \hat{L}_z |[N]_{n_a LM}\rangle = M |[N]_{n_a LM}\rangle, \]

explicitly given by

\[ |[N]; n_a LM\rangle = C_{Nn_p L} (s^\dagger)^{N-n_a} (a^\dagger \cdot \hat{a}^\dagger)^{(n_a-L)/2} \gamma^L_M (\hat{a}^\dagger) |0\rangle. \]

with branching rules

\[ n_a = 0, 1, \ldots, N; \quad L = n_a, n_a - 2, \ldots, 1 \text{ or } 0; \quad -L \leq M \leq L. \]

\( U(3) \) basis versus harmonic oscillator basis

\[ \sum_{n_a} \sum_{L, M} |[N]_{n_a LM}\rangle \langle [N]_{n_a LM}| = 1, \]

\[ \sum_{n} \sum_{l, m} |nlm\rangle \langle nlm| = 1 \]
We propose the mapping

\[|nlm\rangle \leftrightarrow |[N];n_aLM\rangle; \quad n_a = 0, 1, \ldots, N. \]  

(19)

with \( n \leftrightarrow n_a; \ l \leftrightarrow L \) and \( m \leftrightarrow M \).

We introduce the density operator

\[\hat{\rho} = \sum_{nlm} p_{nlm} |nlm\rangle \langle nlm| \approx \sum_{n_a=0}^{N} \sum_{LM} p_{n_aLM} |[N];n_aLM\rangle \langle [N];n_aLM|,\]  

(20)

with \( p_{nlm} = p_{n_aLM} \) and normalization \( \sum_{n=0}^{N} \sum_{lm} p_{nlm} = 1 \).

Algebraic realization of \( \hat{F}_{cs} \)

\[\hat{F}_{alg} \approx \sum_{s,m} \alpha_s^{(m)}(F_{cs}) \hat{Y}_s \hat{P}_m,\]  

(21)

where \( |m\rangle \rightarrow |[N];n_aLM\rangle \), \( \hat{Y}_s \) are generators of the \( U(4) \) group, \( \hat{P}_m \) are projection operators.

\[\hat{P}_m = |[N];n_aLM\rangle \langle [N];n_aLM|,\]  

(22)
The state dependent coefficients $\alpha^{(m)}_s(F_{cs})$ are determined through the set of equations

$$
\sum_s \alpha^{(m)}_s(F_{cs}) \langle m|\hat{Y}_r \hat{\rho} \hat{Y}_s|m\rangle = \langle m|\hat{Y}_r \hat{\rho} \hat{F}_{cs}|m\rangle.
$$

(23)

Consider the expansion with

$$
Y_1 = a^\dagger_{\mu} s, \quad Y_2 = s^\dagger \tilde{a}_{\mu}.
$$

(24)

We obtain

$$
\hat{Q}_{\mu} = \frac{\lambda_0}{\sqrt{2N}} (a^\dagger_{\mu} s - s^\dagger \tilde{a}_{\mu}) = \frac{\lambda_0}{\sqrt{2N}} \hat{D}_{\mu},
$$

(25a)

$$
\hat{P}_{-\mu} = -i(-)^{1-\mu} \frac{\hbar}{\lambda_0} \frac{1}{\sqrt{2N}} (a^\dagger_{\mu} s + s^\dagger \tilde{a}_{\mu})
= -(-)^{1-\mu} \frac{\hbar}{\lambda_0} \frac{1}{\sqrt{2N}} \hat{R}_{\mu}.
$$

(25b)

Anharmonization procedure

$$
q_{\mu} \bigg|_{a_{\mu} \rightarrow b_{\mu}} \rightarrow Q_{\mu}; \quad p_{\mu} \bigg|_{a_{\mu} \rightarrow b_{\mu}} \rightarrow P_{\mu}.
$$

(26)
Algebraic Hamiltonian

\[ \hat{H}_{alg}^{U(4)} = \frac{1}{2m} \mathcal{P}^2 + \frac{\omega^2 m}{2} \mathcal{Q}^2. \quad (27) \]

in terms of the generators

\[ \hat{H}_{alg}^{U(4)} = \frac{\hbar \omega}{4} \left[ \frac{R^2 + D^2}{N} \right]. \quad (28) \]

which can be recast in the following form

\[ \hat{H}_{alg}^{U(4)} = \hbar \omega \left[ \left( 1 - \frac{1}{N} \right) \hat{n}_a + \frac{3}{2} - \frac{\hat{n}_a^2}{N} \right]. \quad (29) \]

This result leads to the identification of the \( U(3) \) chain as the energy representation with eigenkets

\[ \hat{n}_a | [N] n_a LM \rangle = n_a | [N] n_a LM \rangle. \quad (30) \]
For $SO(4)$ we have $\hat{C}_{SO(4)} = \hat{D}^2 + L^2$, and consequently

$$\hat{C}_{SO(4)} = \hat{W}^2 = N \frac{2m\omega}{\hbar} Q^2 + \hat{L}^2.$$ (31)

In similar form we have

$$\hat{C}_{SO(4)} = \hat{W}^2 = N \frac{2}{\hbar m\omega} P^2 + \hat{L}^2,$$ (32)

with $\hat{C}_{SO(4)} = \hat{R}^2 + L^2$.

Identification of the dynamical symmetries according to energy, coordinates and momenta representation.

<table>
<thead>
<tr>
<th>Chain</th>
<th>Basis</th>
<th>Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U(4) \supset U(3) \supset SO(3) \supset SO(2)$</td>
<td>$[N]n_{a}LM$</td>
<td>Energy</td>
</tr>
<tr>
<td>$U(4) \supset SO(4) \supset SO(3) \supset SO(2)$</td>
<td>$[N]\zeta LM$</td>
<td>Coordinates</td>
</tr>
<tr>
<td>$U(4) \supset \overline{SO(4)} \supset SO(3) \supset SO(2)$</td>
<td>$[N]\bar{\zeta} LM$</td>
<td>Momenta</td>
</tr>
</tbody>
</table>

The corresponding eigenvectors associated with the coordinates and momenta representations satisfy

$$\hat{W}^2 [N]\zeta LM \rangle = \zeta(\zeta + 2) [N]\zeta LM \rangle,$$ (33a)

$$\hat{W}^2 [N]\bar{\zeta} LM \rangle = \bar{\zeta}(\bar{\zeta} + 2) [N]\bar{\zeta} LM \rangle,$$ (33b)

with branching rules $\zeta, \bar{\zeta} = N, N - 2, \ldots, 1$ or 0, and $L = 0, 1, \ldots, \zeta(\bar{\zeta})$. 
Algebraic representation of 3D systems

3D Hamiltonian:

$$\hat{H} = \frac{1}{2m} \hat{p}^2 + V(\sqrt{\hat{q}^2}).$$  \hfill (34)

The corresponding algebraic Hamiltonian is:

$$H_{alg}^{U(4)} = \hat{H} \bigg|_{\hat{q} \to Q, \hat{p} \to P} = \frac{1}{2m} P^2 + V(\sqrt{Q^2}).$$  \hfill (35)

A practical convenient form is:

$$H_{alg}^{U(4)} = \hbar \omega \left[ \left( 1 - \frac{1}{N} \right) \hat{n}_a + \frac{3}{2} - \frac{\hat{n}_a^2}{N} \right] + \epsilon V'(\sqrt{Q^2}).$$  \hfill (36)

where

$$V'(\sqrt{Q^2}) = -\frac{m \omega^2}{2} Q^2 + V(\sqrt{Q^2}),$$  \hfill (37)

with $\epsilon [0, 1]$. Taking into account the scalar character of $Q^2$

$$\langle [N] \zeta' LM | Q^2 | [N] \zeta LM \rangle = \frac{\lambda_0^2}{2} \frac{[\zeta(\zeta + 2) - L(L + 1)]}{N} \delta_{\zeta', \zeta}. \hfill (38)$$
Hence the matrix elements of the Hamiltonian (for a given $L$) in the energy representation take the general form

$$H^{(E)} = \Lambda^{(E)} + \epsilon T^\dagger \Lambda^{(Q)} T,$$

where

$$||\Lambda^{(E)}|| = \hbar \omega \left[ \left( 1 - \frac{1}{N} \right) \hat{n}_a + \frac{3}{2} - \frac{\hat{n}_a^2}{N} \right] \delta_{n'_a, n_a},$$

$$||\Lambda^{(Q)}|| = \hbar \omega \left[ - \frac{1}{2} \frac{\xi(\zeta, L)^2}{2N} + \frac{1}{\hbar \omega} V \left( \lambda_0 \frac{\xi(\zeta, L)}{\sqrt{2N}} \right) \right] \delta_{\zeta, \zeta'},$$

with $\xi(\zeta, L) = \sqrt{\zeta(\zeta + 2)} - L(L + 1)$. The $T$ matrix stands for the transformation brackets: $T = ||\langle [N] \zeta LM | [N] n_a LM \rangle||$.
Consider as an example the Morse potential

\[ V'(Q) = -\frac{m\omega^2}{2}Q^2 + D(1 - \exp[-\beta(\sqrt{Q^2} - r_0)])^2, \]  

(42)

with matrix representation

\[ ||\Lambda^{(Q)}|| = \left[ -\frac{1}{2} \frac{\xi(\zeta, L)^2}{2N} + \bar{D} \left(1 - e^{-\bar{\beta} \left(\sqrt{\frac{1}{2N}} \xi(\zeta, L) - \bar{r}_0\right)}\right)^2 \right] \delta_{\zeta, \zeta'}. \]  

(43)

We have taken \( \hbar \omega \) and \( \lambda_0 = \sqrt{\hbar/(m\omega)} \) for energy and length units respectively. In these units the following relations are satisfied

\[ \bar{\beta} = \sqrt{\frac{1}{2\bar{D}}}; \quad \kappa = 2j + 1 = 4\bar{D}, \]  

(44)

where the bar refers to dimensionless coordinates. As a particular system we consider the following parameters :

\[ j = 9; \quad \bar{D} = 4.75; \quad \bar{\beta} = \sqrt{\frac{1}{2 \times 4.75}}, \]  

(45)
Correlation diagram from the harmonic oscillator ($\epsilon = 0$) to the Morse potential ($\epsilon = 1$). To simplify only the levels with $L = 0, 1, 2, 3$ have been included just to show the rotational bands induced by the displaced potential. The parameters were taken to be (45) together with $N = 2500$. 
Rotational bands emerged from the displaced Morse oscillator for $\epsilon = 1$. To simplify only the levels with $L = 0, 1, 2, 3$ have been included. The parameters were taken to be (45) together with $N = 2500$. 
In our approach the $|\psi_{v,LM}^N\rangle$ eigenstate takes thus the form

$$|\psi_{v,LM}^N\rangle = \sum_{n_a=0}^{N} \langle [N] n_a LM | \psi_{v,LM}^N \rangle | [N] n_a LM \rangle,$$

(46)

with $v = 0, 1, \ldots, j - 1$.

Comparison between analytic (dashed line) and calculated (continuous line) radial wave function $\langle \bar{r} | \Psi_{5,0}^{N=2500} \rangle$ and $\langle \bar{r} | \Psi_{8,0}^{N=2500} \rangle$ for the Morse potential using (39) with parameters (45) for $N = 2500$ and $\epsilon = 1$. As expected for small $r$ the analytic solution is not valid.
Calculated radial wave functions $\langle \vec{r} | \Psi_{5,L}^{N=2500} \rangle$ and $\langle \vec{r} | \Psi_{8,L}^{N=2500} \rangle$ for the Morse potential using (39) with parameters (45) for $N = 2500$ and $\epsilon = 1$, corresponding to angular momenta $L = 0, 1, 2, 3$. 
For the dipole transitions the intensities $I(vL \rightarrow v'L')$ are:

$$I(vL \rightarrow v'L') \approx \sum_{MM'} |\langle \Psi_{v'L'M'} | \hat{T}^{(1)}_{\lambda} | \Psi_{vLM} \rangle|^2$$

$$= (2L' + 1) |\langle \Psi_{v'L'} | \hat{T}^{(1)}_{\lambda} | \Psi_{vL} \rangle|^2. \quad (47)$$

The explicit form of the dipole operators is

$$\hat{T}^{(1)}_{\lambda} = Q_{\lambda} \mu_e(r), \quad (48)$$

where a reasonable proposal is

$$\mu_e(r) = e^{-\gamma r}. \quad (49)$$

In our formalism the matrix elements are recast in matrix form in the following form

$$\langle \Psi_{v'L'} || \hat{T}^{(1)} || \Psi_{vLM} \rangle = C^{L'}_v Q \mathbf{T}^\dagger \Lambda^{(\mu_e)} \mathbf{T} (C^L_v)^\dagger, \quad (50)$$

where

$$||\Lambda^{(\mu_e)}|| = \left[ e^{-\frac{\gamma}{2N}} \xi(\zeta,L) \right] \delta_{\zeta,\zeta'}. \quad (51)$$

The matrix $Q$ corresponds to

$$||Q|| = ||\langle [N]n'L' || Q^{(1)} || [N]n''L \rangle||. \quad (52)$$
Plot corresponding to \( \log(I(0L \rightarrow vL + 1)) \) vs \( v \) for the cases \( L = 0, 1, 2 \). The dipole function \( \mu_e \) was taken to be (49) with \( \bar{\gamma} = 1 \).
Let us now consider the rotational spectrum

Rotational spectrum showing the $P$ and $R$ branches for the vibrational transition $0 \rightarrow 1$. The $R$-branch shows the band head, a turning point in the spectrum.
A realistic case: $\text{O}_2$

A potential energy surface (PES) obtained for $\text{O}_2$ can be modeled as an expansion

$$V(r) = \sum_{k=0}^{7} a_k \exp\left[-\alpha \beta^k r^2\right].$$

(53)

The units are: $\alpha$ in $\text{Å}^{-2}$, $\beta$ is dimensionless, and $a_k$ are in miliHartree.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.785</td>
<td>1.307</td>
<td>-2388.5641690</td>
<td>18086.977116</td>
<td>-71760.197585</td>
<td>154738.09175</td>
</tr>
<tr>
<td>$a_4$</td>
<td>$a_5$</td>
<td>$a_6$</td>
<td>$a_7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-215074.85646</td>
<td>214799.54567</td>
<td>-148395.42850</td>
<td>73310.78145</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Graphs of potential energy surface](image)
A realistic case: $O_2$ Vibrational states

Vibrational states

Vibrational term values $G_{v+1} - G_0$ (in cm$^{-1}$) for $O_2$ as obtained by: i) Ref. [1] (black line), ii) this work (green line), and iii) the known experimental data (red dots).

Vibrational energy spacings $G_{v+1} - G_v$ (in cm$^{-1}$) for $O_2$ as obtained by: i) Ref. [1] (black line), ii) this work (green line), and iii) the known experimental data (red dots).

Rotational states

In Ref. [1] the spectroscopic rotational factors $B_v$ and $D_v$ are calculated and compared to experimental data. These factors are obtained by a linear regression of $\frac{F_v}{L(L+1)}$ vs $L(L+1)$ for $L$ from 0 to 10 for each $v$–value using

$$\frac{F_v}{L(L+1)} = \frac{E_{v,L} - E_{v,o}}{L(L+1)} = B_v - D_v L(L+1).$$

Rotational constant $B_v$ (in cm$^{-1}$) as a function of $v$ for O$_2$: i) experimental (red dots), ii) calculation in Ref. [1], and iii) present results (green line).

Rotational centrifugal constant $D_v$ (in 10$^{-6}$ cm$^{-1}$) as a function of $v$ for O$_2$: i) experimental (red dots), ii) calculation in Ref. [1], and iii) present results (green line).
Conclusions

- The Unitary Group Approach provides a simple methodology to describe 3D systems in a purely algebraic scheme.
- The key to be able to apply this approach to general potentials is the identification of the bases in coordinate and momentum representations.
- The transformation brackets are calculated only once for a given $N$, giving a method to obtain solutions for different potentials in a simple way.
- Our approach represents an algebraic approach with a clear connection with configuration space, taking advantage of the additional bases to simplify the description.

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