Unitary group approach for effective potentials in 3D systems

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Content

3D harmonic oscillator

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

The corresponding eigenfunctions are

$$\Psi_{nlm}(q,\theta,\phi) = A_{nl}\ q^l e^{-q^2/2} L^{l+1/2}_{(n-l)/2}(q^2) Y^l_m(\theta,\phi). \tag{2}$$

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In the Fock space

$$a^\dagger_\mu \quad = \quad \frac{1}{\sqrt{2}}\left(\frac{1}{\lambda_0}q_\mu - i\frac{\lambda_0}{\hbar}(-1)^\mu p_{-\mu}\right); \tag{3a}$$

$$\tag{3b}$$

where $\lambda_0 = \sqrt{\hbar/m\omega}$, $q_\mu(\mu = 1, 0, -1)$, $p_\mu = -i\hbar\frac{\partial}{\partial q_\mu}$, $\tilde{a}_\mu = (-1)^{1-\mu}a_{-\mu}$.
The Hamiltonian takes the form

$$\hat{H}^{h.o.}_{Fock} = \hbar\omega(\hat{n} + 3/2) \tag{4}$$

with $\hat{n} = \sqrt{3}[a^\dagger \times \tilde{a}]^{(0)}_0$, and eigenfunctions

$$|nlm\rangle = B_{nl}\ (\mathbf{a}^\dagger \cdot \hat{\mathbf{a}}^\dagger)^{(n-l)/2} \mathcal{Y}^l_m(\hat{\mathbf{a}}^\dagger)|0\rangle \tag{5}$$

where

$$\mathcal{Y}^l_m(\hat{\mathbf{a}}^\dagger) = 2^{-l/2}(\hat{\mathbf{a}}^\dagger \cdot \hat{\mathbf{a}}^\dagger)^{l/2} Y^l_m(\hat{\mathbf{a}}^\dagger). \tag{6}$$

Unitary Group Approach

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

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

$$\hat{n}_a = \sqrt{3}[a^\dagger \times \tilde{a}]^{(0)}_0; \qquad \hat{n}_s = s^\dagger s, \tag{7a}$$

$$\hat{L}_\mu = \sqrt{2}[a^\dagger \times \tilde{a}]^{(1)}_\mu; \qquad \hat{D}_\mu = a^\dagger_\mu s - s^\dagger \tilde{a}_\mu, \tag{7b}$$

$$\hat{Q}_\mu = [a^\dagger \times \tilde{a}]^{(2)}_\mu; \qquad \hat{R}_\mu = i(a^\dagger_\mu s + s^\dagger \tilde{a}_\mu). \tag{7c}$$

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

$$U(4) \supset U(3) \supset SO(3) \supset SO(2), \tag{8a}$$

$$U(4) \supset SO(4) \supset SO(3) \supset SO(2), \tag{8b}$$

$$U(4) \supset \overline{SO}(4) \supset SO(3) \supset SO(2), \tag{8c}$$

with the following generators

$$G_{U(3)} = \{\hat{n}_a, \hat{L}_\mu, \hat{Q}_\mu\}, \tag{9a}$$

$$G_{SO(4)} = \{\hat{D}_\mu, \hat{L}_\mu\}, \tag{9b}$$

$$G_{\overline{SO}(4)} = \{\hat{R}_\mu, \hat{L}_\mu\}. \tag{9c}$$

F.Iachello and R.D.Levine, Algebraic Theory of Molecules. Oxford University Press. 1995

$U(3)$ basis

$$U(4) \supset U(3) \supset SO(3) \supset SO(2) \tag{10}$$

The CSCO associated with this chain establishes the basis

$$\hat{N}|[N]n_a LM\rangle = N\ |[N]n_a LM\rangle \tag{11}$$
$$\hat{n}_a|[N]n_a LM\rangle = n_a\ |[N]n_a LM\rangle \tag{12}$$
$$\hat{L}^2|[N]n_a LM\rangle = L(L+1)\ |[N]n_a LM\rangle \tag{13}$$
$$\hat{L}_z|[N]n_a LM\rangle = M\ |[N]n_a LM\rangle, \tag{14}$$

explicitly given by

$$|[N]; n_a LM\rangle = C_{N n_p L}\ (s^\dagger)^{N-n_a}(\mathbf{a}^\dagger \cdot \hat{\mathbf{a}}^\dagger)^{(n_a-L)/2}\mathcal{Y}^L_M(\hat{\mathbf{a}}^\dagger)|0\rangle. \tag{15}$$

with branching rules

$$n_a = 0, 1, \ldots, N; \qquad L = n_a, n_a - 2, \ldots, 1 \text{ or } 0; \qquad -L \leq M \leq L. \tag{16}$$

$U(3)$ basis versus harmonic oscillator basis

$$\sum_{n_a}^{N} \sum_{L,M} |[N]n_a LM\rangle\langle[N]n_a LM| = 1, \tag{17}$$

$$\sum_{n}^{\infty} \sum_{l,m} |nlm\rangle\langle nlm| = 1 \tag{18}$$

Connection between algebraic and configuration space

We propose the mapping

$$|nlm\rangle \leftrightarrow |[N]; n_a LM\rangle; \quad n_a = 0, 1, \ldots, N. \tag{19}$$

with $n \leftrightarrow n_a; l \leftrightarrow L$ and $m \leftrightarrow M$.
We introduce the density operator

$$\hat{\rho} = \sum_{nlm} p_{nlm} |nlm\rangle\langle nlm| \approx \sum_{n_a=0}^{N} \sum_{LM} p_{n_a LM} \; |[N]; n_a LM\rangle\langle [N]; n_a LM|, \tag{20}$$

with $p_{nlm} = p_{n_a LM}$ and normalization $\sum_{n=0}^{N} \sum_{lm} \; p_{nlm} = 1$.

Algebraic realization of $\hat{\mathcal{F}}_{cs}$

$$\hat{\mathcal{F}}_{alg} \approx \sum_{s,m} \alpha_s^{(m)}(\mathcal{F}_{cs}) \; \hat{Y}_s \hat{P}_m, \tag{21}$$

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

$$\hat{P}_m = |[N]; n_a LM\rangle\langle [N]; n_a LM|, \tag{22}$$

R.D.Santiago et al, Mol.Phys.24 (2017) 3206

The state dependent coefficients $\alpha_s^{(m)}(\mathcal{F}_{cs})$ are determined through the set of equations

$$\sum_s \alpha_s^{(m)}(\mathcal{F}_{cs})\ \langle m|\hat{Y}_r^\dagger \hat{\rho} \hat{Y}_s|m\rangle = \langle m|\hat{Y}_r^\dagger \hat{\rho} \hat{\mathcal{F}}_{cs}|m\rangle. \tag{23}$$

Consider the expansion with

$$Y_1 = a_\mu^\dagger s, \quad Y_2 = s^\dagger \tilde{a}_\mu. \tag{24}$$

We obtain

$$\hat{\mathcal{Q}}_\mu = \frac{\lambda_0}{\sqrt{2N}}(\ a_\mu^\dagger s - s^\dagger \tilde{a}_\mu) = \frac{\lambda_0}{\sqrt{2N}} \hat{D}_\mu, \tag{25a}$$

$$\begin{aligned} \hat{\mathcal{P}}_{-\mu} &= -i(-)^{1-\mu} \frac{\hbar}{\lambda_0} \frac{1}{\sqrt{2N}}(\ a_\mu^\dagger s + s^\dagger \tilde{a}_\mu) \\ &= -(-)^{1-\mu} \frac{\hbar}{\lambda_0} \frac{1}{\sqrt{2N}} \hat{R}_\mu. \end{aligned} \tag{25b}$$

Anharmonization procedure

$$q_\mu\Big|_{a_\mu \to b_\mu} \to \mathcal{Q}_\mu; \qquad p_\mu\Big|_{a_\mu \to b_\mu} \to \mathcal{P}_\mu. \tag{26}$$

Energy, coordinates and momenta representations

Algebraic Hamiltonian

$$\hat{H}^{\mathsf{U(4)}}_{alg} = \frac{1}{2m}\,\mathcal{P}^2 + \frac{\omega^2 m}{2}\,\mathcal{Q}^2. \tag{27}$$

in terms of the generators

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

which can be recast in the following form

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

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

$$\hat{n}_a|[N]n_aLM\rangle = n_a|[N]n_aLM\rangle. \tag{30}$$

For $SO(4)$ we have $\hat{C}_{SO(4)} = \hat{D}^2 + L^2$, and consequently

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

In similar form we have

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

with $\hat{C}_{\overline{SO}(4)} = \hat{R}^2 + L^2$.
Identification of the dynamical symmetries according to energy, coordinates and momenta representation.

Chain	Basis	Representation
$U(4) \supset U(3) \supset SO(3) \supset SO(2)$	$\|[N]n_a LM\rangle$	Energy
$U(4) \supset SO(4) \supset SO(3) \supset SO(2)$	$\|[N]\zeta LM\rangle$	Coordinates
$U(4) \supset \overline{SO}(4) \supset SO(3) \supset SO(2)$	$\|[N]\bar{\zeta} LM\rangle$	Momenta

The corresponding eigenvectors associated with the coordinates and momenta representations satisfy

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

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

with braching 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:

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

The corresponding algebraic Hamiltonian is:

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

A practical convenient form is:

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

where

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

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

$$\langle [N]\zeta' LM|\mathcal{Q}^2|[N]\zeta LM\rangle = \frac{\lambda_0^2}{2}\frac{[\zeta(\zeta+2)-L(L+1)]}{N}\ \delta_{\zeta',\zeta}. \tag{38}$$

Hence the matrix elements of the Hamiltonian (for a given L) in the energy representation take the general form

$$\mathbf{H}^{(E)} = \mathbf{\Lambda}^{(E)} + \epsilon \mathbf{T}^{\dagger} \mathbf{\Lambda}^{(Q)} \mathbf{T}, \tag{39}$$

where

$$||\mathbf{\Lambda}^{(E)}|| = \hbar\omega \left[\left(1 - \frac{1}{N} \right) \hat{n}_a + \frac{3}{2} - \frac{\hat{n}_a^2}{N} \right] \delta_{n'_a, n_a}, \tag{40}$$

$$||\mathbf{\Lambda}^{(Q)}|| = \hbar\omega \left[-\frac{1}{2} \frac{\xi(\zeta, L)^2}{2N} + \frac{1}{\hbar\omega} V \left(\lambda_0 \frac{\xi(\zeta, L)}{\sqrt{2N}} \right) \right] \delta_{\zeta, \zeta'}, \tag{41}$$

with $\xi(\zeta, L) = \sqrt{\zeta(\zeta+2) - L(L+1)}$. The $\mathbf{T}$ matrix stands for the transformation brackets: $\mathbf{T} = ||\langle [N] \zeta L M | [N] n_a L M \rangle||$

Consider as an example the Morse potential

$$V'(\mathcal{Q}) = -\frac{m\omega^2}{2}\mathcal{Q}^2 + D(1-\exp[-\beta(\sqrt{\mathcal{Q}^2}-r_0)])^2, \tag{42}$$

with matrix representation

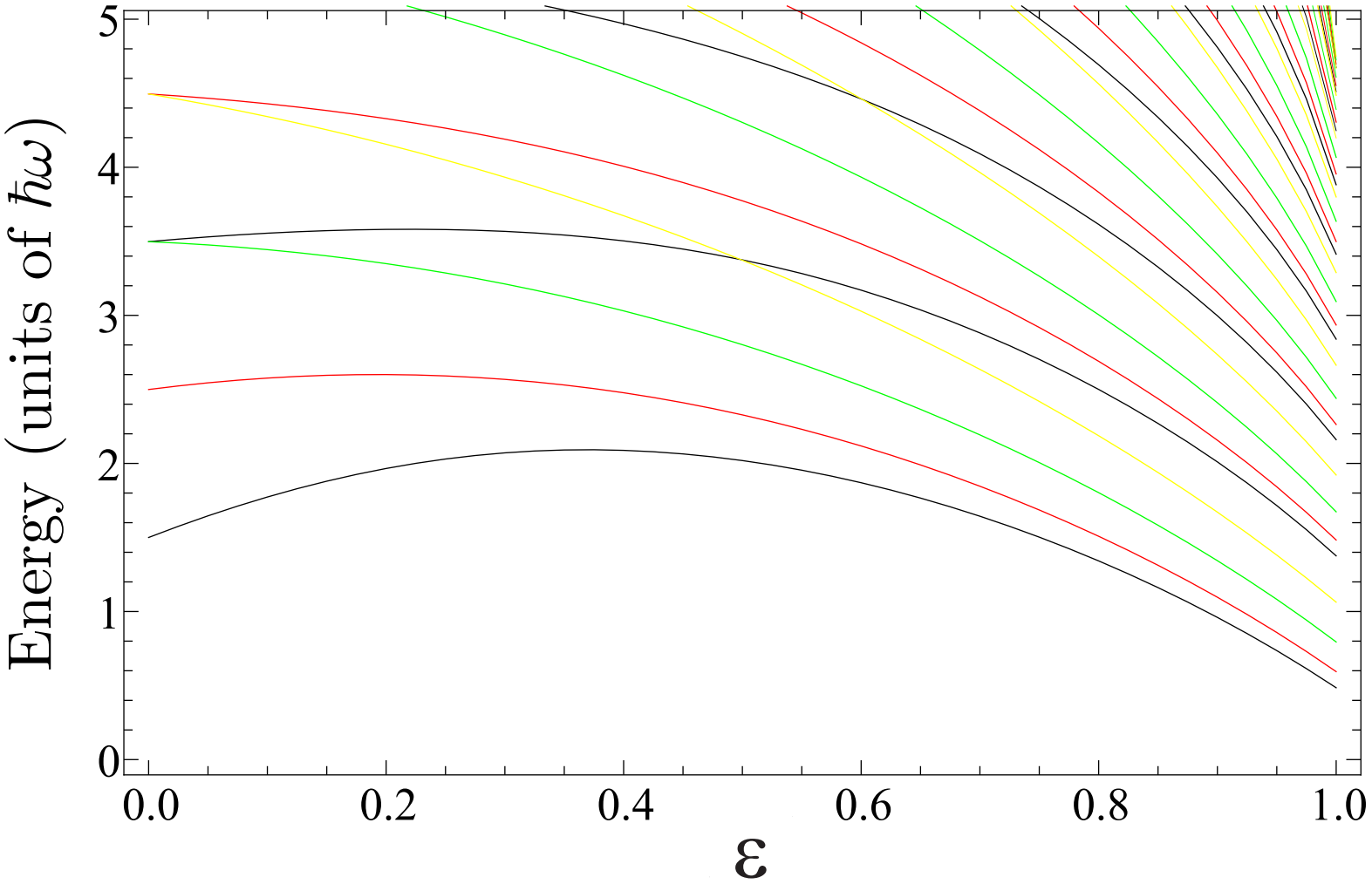
$$||\mathbf{\Lambda}^{(Q)}|| = \left[-\frac{1}{2}\frac{\xi(\zeta,L)^2}{2N} + \bar{D}\left(1-e^{-\bar{\beta}\left(\sqrt{\frac{1}{2N}}\xi(\zeta,L)-\bar{r}_0\right)}\right)^2 \right]\delta_{\zeta,\zeta'}. \tag{43}$$

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

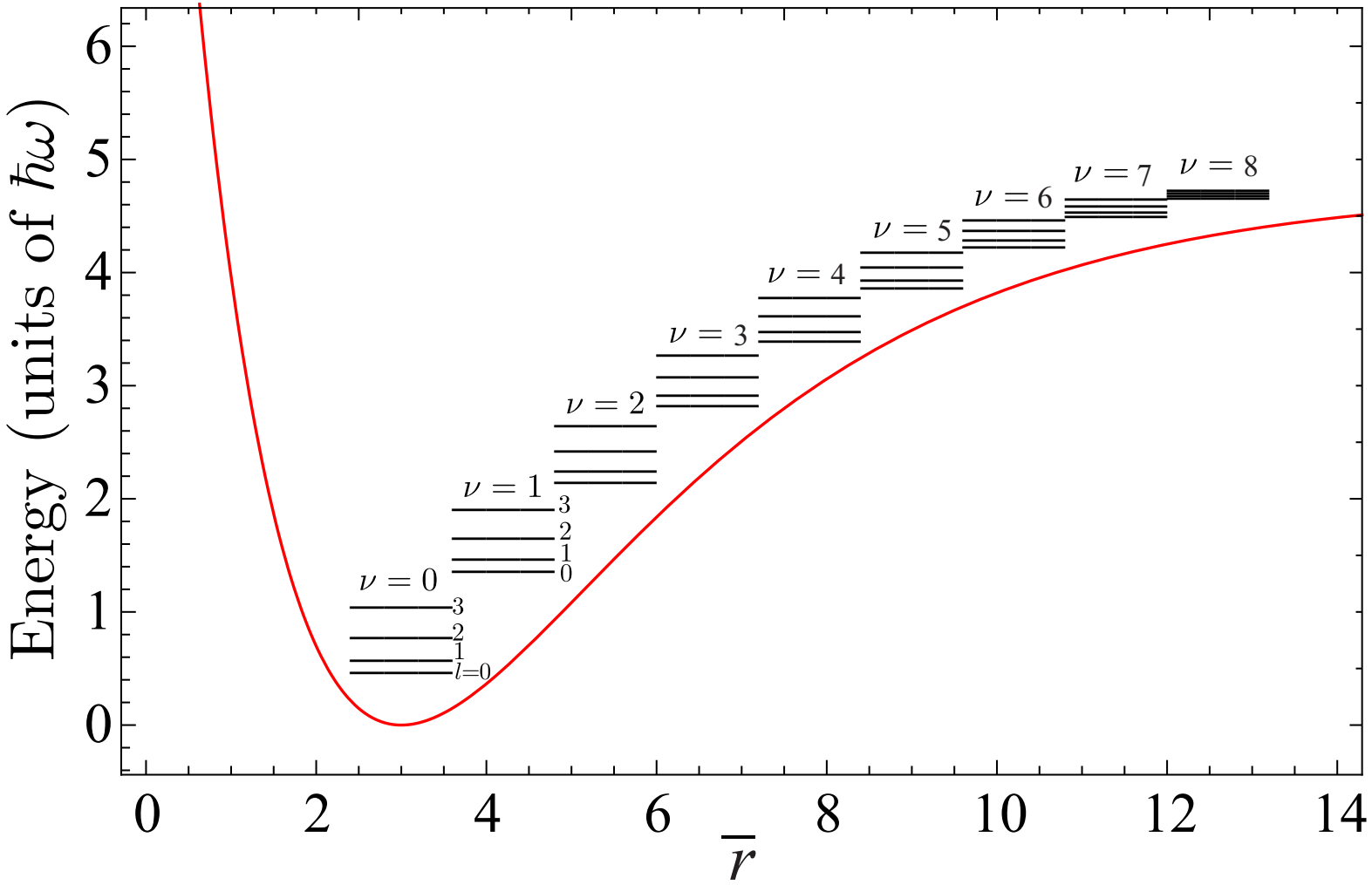
$$\bar{\beta} = \sqrt{\frac{1}{2\bar{D}}}; \quad \kappa = 2j+1 = 4\bar{D}, \tag{44}$$

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

$$j = 9; \quad \bar{D} = 4{,}75; \quad \bar{\beta} = \sqrt{\frac{1}{2\times 4{,}75}}, \tag{45}$$



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 $N = 2500$.

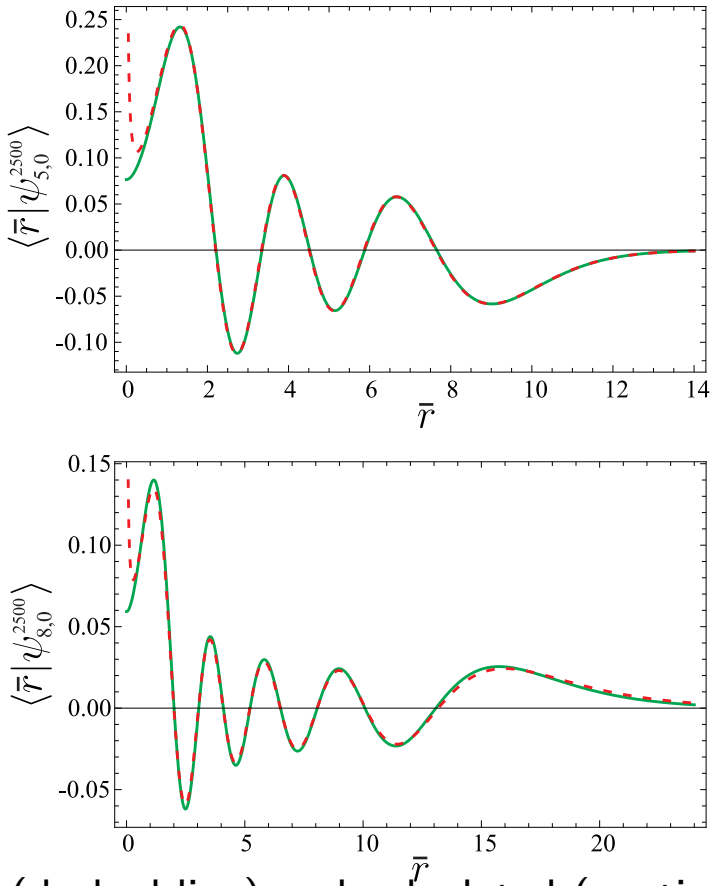


Rotational bands emerged from the displaced Morse oscillator for $\epsilon = 1$. To simplify only the levels with $L = 0, 1, 2, 3$ have been included. The parameters were taken to be (45) together with $N = 2500$.

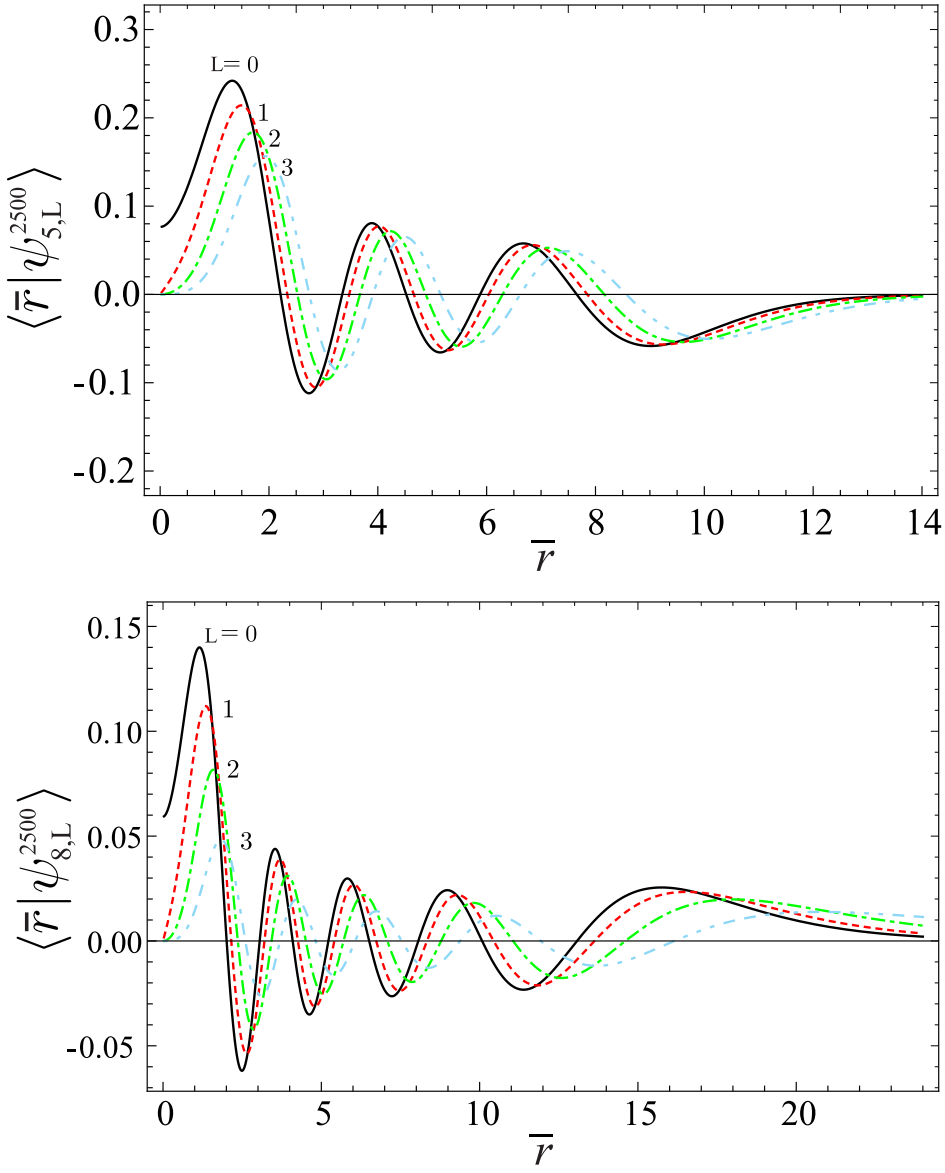
In our approach the $|\psi^N_{v,LM}\rangle$ eigenstate takes thus the form

$$|\psi^N_{v,LM}\rangle = \sum_{n_a=0}^{N} \langle [N] n_a LM | \psi^N_{v,LM}\rangle \; |[N] n_a LM\rangle, \tag{46}$$

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



Comparison between analytic (dashed line) and calculated (continuous line) radial wave function $\langle \bar{r}|\Psi^{N=2500}_{5,0}\rangle$ and $\langle \bar{r}|\Psi^{N=2500}_{8,0}\rangle$ 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 $\langle \bar{r} | \Psi^{N=2500}_{5,L} \rangle$ and $\langle \bar{r} | \Psi^{N=2500}_{8,L} \rangle$ for the Morse potential using (39) with parameters (45) for $N = 2500$ and $\epsilon = 1$, corresponding to angular momenta $L = 0, 1, 2, 3$.

Dipole moment

For the dipole transitions the intensities $I(vL \rightarrow v'L')$ are:

$$\begin{aligned} I(vL \rightarrow v'L') &\approx \sum_{MM'\lambda} |\langle \Psi_{v'L'M'} | \hat{T}^{(1)}_{\lambda} | \Psi_{vLM} \rangle|^2 \\ &= (2L'+1) |\langle \Psi_{v'L'} || \hat{T}^{(1)} || \Psi_{vL} \rangle|^2. \end{aligned} \tag{47}$$

The explicit form of the dipole operators is

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

where a reasonable proposal is

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

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

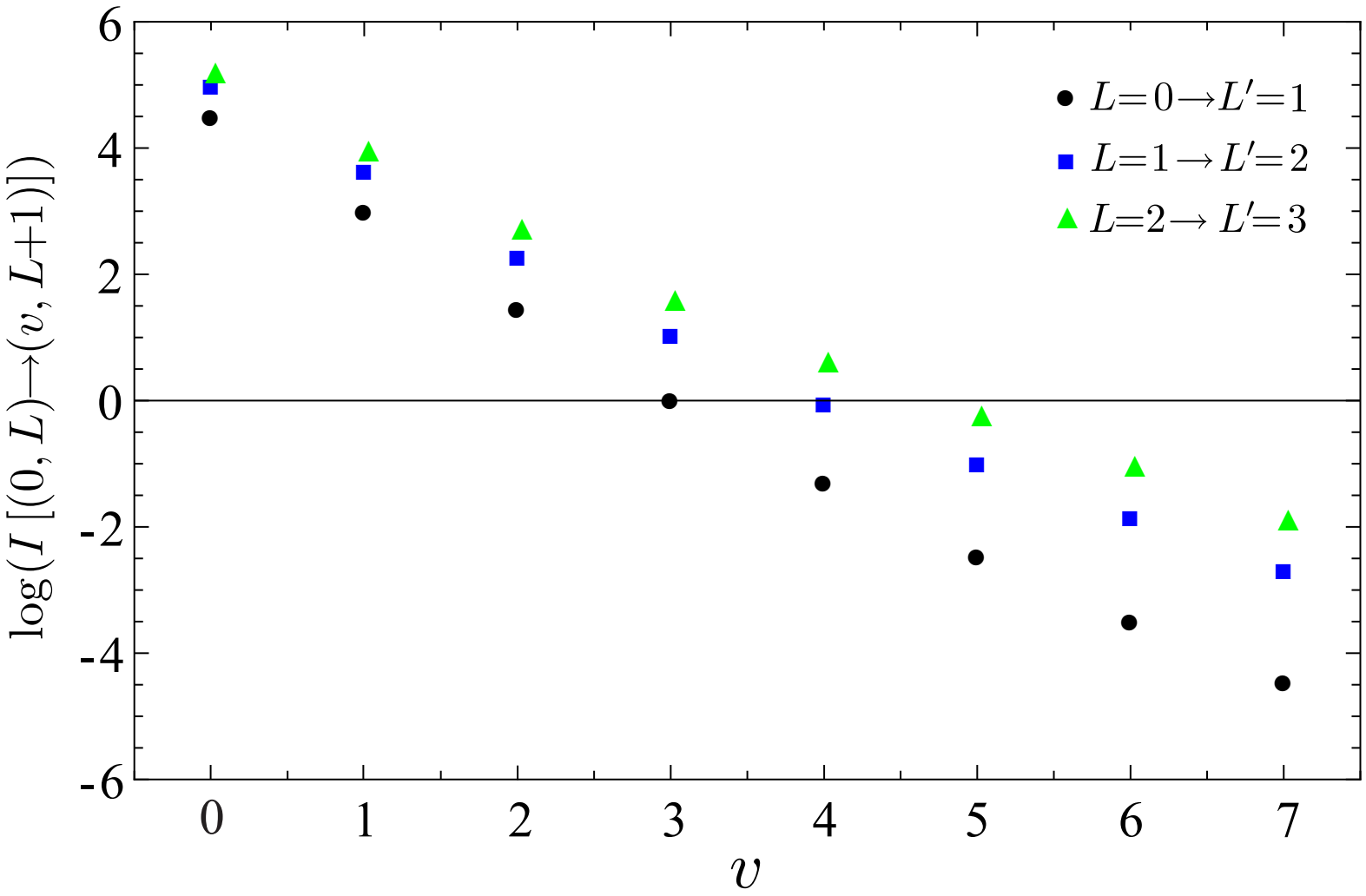
$$\langle \Psi_{v'L'} || \hat{T}^{(1)} || \Psi_{vLM} \rangle = \mathbf{C}^{\mathbf{L}'}_{\mathbf{v}'} \mathbf{Q}\ \mathbf{T}^{\dagger} \mathbf{\Lambda}^{(\mu_e)} \mathbf{T} (\mathbf{C}^{\mathbf{L}}_{\mathbf{v}})^{\dagger}, \tag{50}$$

where

$$||\mathbf{\Lambda}^{(\mu_e)}|| = \left[e^{-\bar{\gamma}\left(\sqrt{\frac{1}{2N}}\xi(\zeta,L)\right)} \right] \delta_{\zeta,\zeta'}. \tag{51}$$

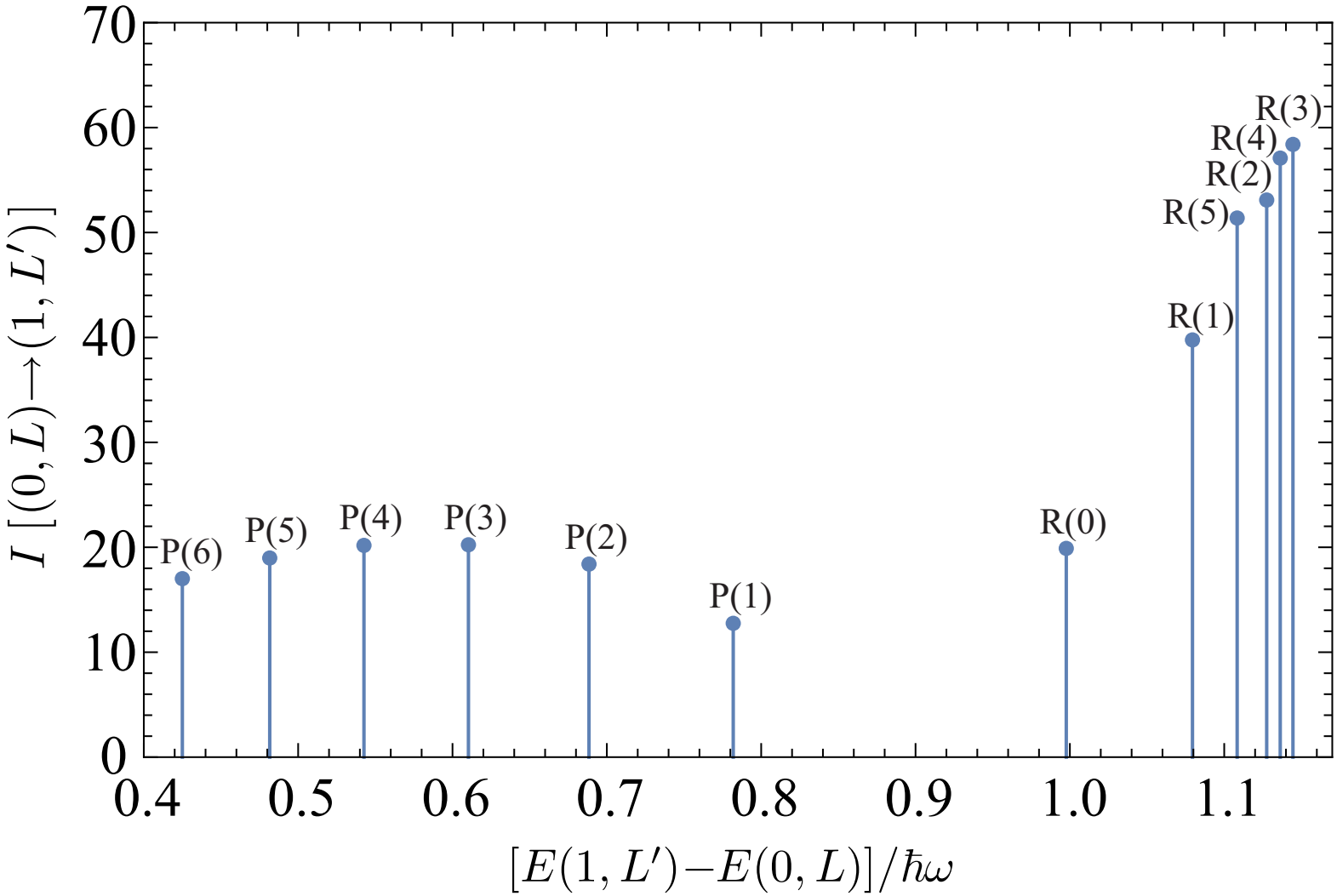
The matrix $\mathbf{Q}$ corresponds to

$$||\mathbf{Q}|| = ||\langle [N] n' L' || Q^{(1)} || [N] n'' L \rangle||. \tag{52}$$



Plot corresponding to $\log(I(0L \rightarrow vL+1))$ vs v for the cases $L = 0, 1, 2$. The dipole function μ_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.

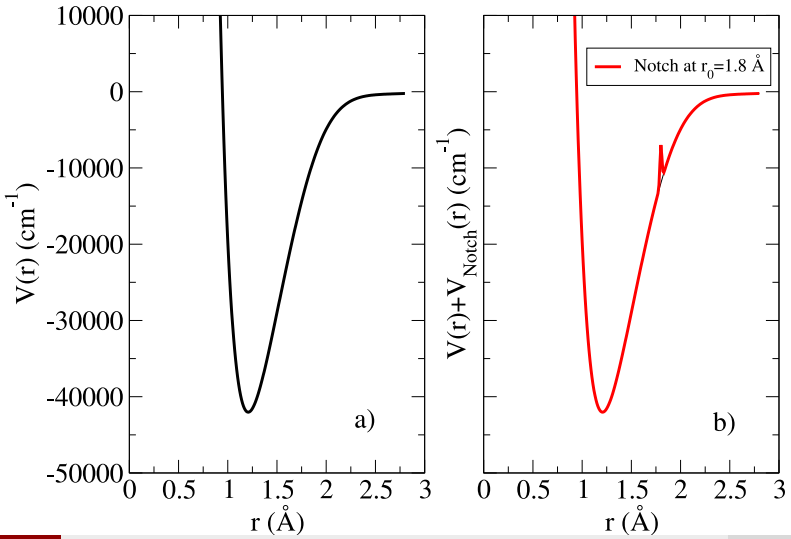
A realistic case: O_2

A potential energy surface (PES) obtained for O_2 can be modeled as an expansion

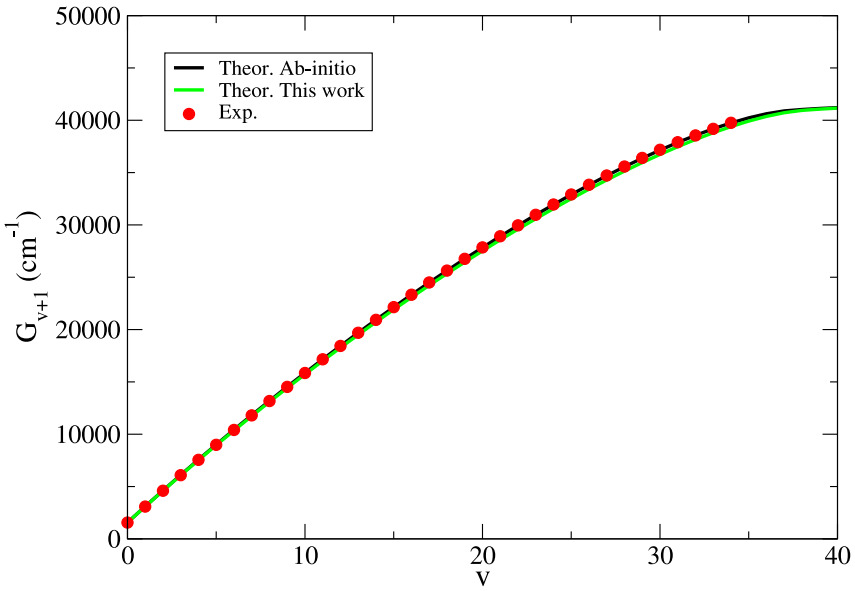
$$V(r) = \sum_{k=0}^{7} a_k \exp\left[-\alpha\beta^k r^2\right]. \tag{53}$$

The units are: α in Å^{-2}, β is dimensionless, and a_k are in miliHartree.

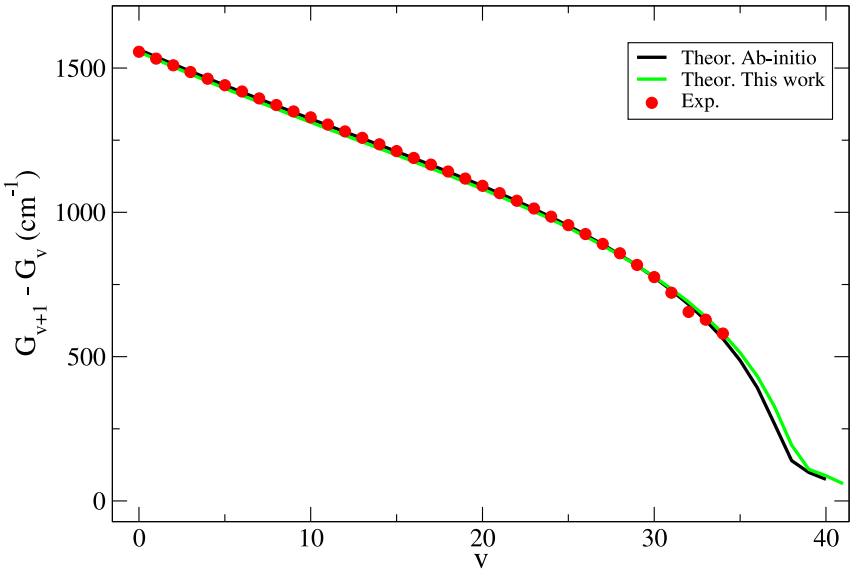
α	β	a_0	a_1	a_2	a_3
0.785	1.307	-2388.5641690	18086.977116	-71760.197585	154738.09175
		a_4	a_5	a_6	a_7
		-215074.85646	214799.54567	-148395.42850	73310.78145



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).



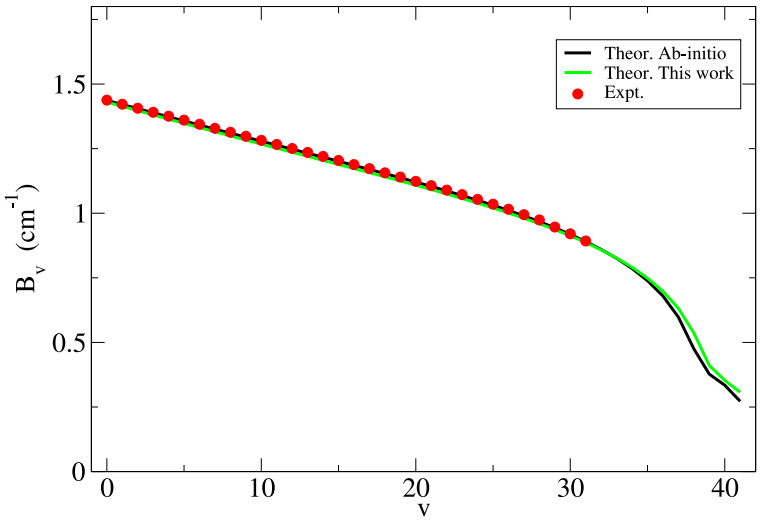
Vibrational energy spacings $G_{v+1} - G_v$ (in cm^{-1}) for O_2 as obtained by:i) Ref.[1] (black line), ii) this work (green line), and iii) the known experimental data (red dots).

[1] L. Bytautas et al, J. Chem. Phys. 132 (2010) 074307

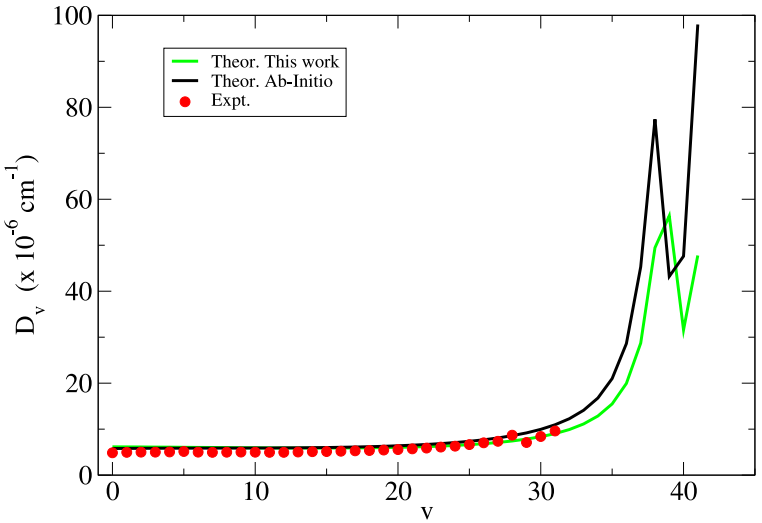
Rotational states

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

$$\frac{F_v}{L(L+1)} = \frac{E_{v,L} - E_{v,o}}{L(L+1)} = B_v - D_v L(L+1). \tag{54}$$



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 asimple way.
- Our approach represents an algebraic approach with a clear connection with configuration space, taking advantage of the additional bases to simplify the description

M. Rodríguez-Arcos et al, Mol.Phys. Submitted