Inter-dimensional degeneracies in van der Waals clusters

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LaTeX with `prosper.sty` does it all.
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Basic definitions

- N atom cluster in D dimensions; positions given by $D \times N$ matrix of Cartesian coordinates

$$\mathbf{R} = (\mathbf{r}_1 \mathbf{r}_2 \ldots \mathbf{r}_N),$$

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$$\mathbf{r}_i = \begin{pmatrix} x_{1i} \\ \vdots \\ x_{Di} \end{pmatrix}.$$

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- Define difference vectors and their lengths
$$\begin{aligned} \mathbf{r}_{ij} &= \mathbf{r}_j - \mathbf{r}_i, \\ r_{ij} &= |\mathbf{r}_{ij}|. \end{aligned}$$

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- Dimensionless Hamiltonian of N bosonic van der Waals atoms with atomic mass μ

$$H = -\frac{1}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{(i,j)} V(r_{ij}),$$

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- Inverse dimensionless mass is $m^{-1} = \hbar^2 / 2^{\frac{1}{3}} \mu \sigma^2 \epsilon$ proportional to the square of the de Boer parameter[1]; ϵ and σ the standard Lennard-Jones parameters. [J. de Boer, *Physica*, **14**, 139 (1948)]

Monte Carlo trial function optimization

- Generate a sample of configurations $\mathbf{R}_\sigma$ $(\sigma = 1, \ldots, s)$ from a relative probability density function $\psi_g(\mathbf{R}_\sigma)^2$.

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- Re-weighted functions defined as $\hat{\beta}_i(R) = \psi_g(R)^{-1}\beta_i(R)$ and $\hat{\beta}'_i(R) = \psi_g(R)^{-1}H\beta_i(R)$ for least-squares.

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- In theory, for a complete set of elementary basis functions β_i the Schrödinger equation becomes

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- In practice, solve for matrix $\mathcal{E}$ in least-squares sense on Monte Carlo sample. Reproduces stationarity of energy w.r.t. linear parameters for infinite sample.

Monte Carlo trial function optimization

- Optimal linear combinations of the basis functions β_i computed by spectral decomposition of $\mathcal{E}$:

$$\mathcal{E}_{ij} = \sum_{k=1}^{n} d_i^k \, \tilde{E}_k \hat{d}_j^k$$

with $\hat{d}_j^k$ and d_i^k left and right eigenvectors of $\mathcal{E}$ with eigenvalues $\tilde{E}_k$.

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- Yield: trial functions

$$\tilde{\psi}^k = \sum_{i=1}^{n} d_i^k \beta_i .$$

Monte Carlo trial function optimization

- Non-linear parameters of the β_i are optimized by minimizing the variance of the local energy of the linearly optimized $\tilde{\psi}^k$

$$\chi^2 = \frac{\sum_{\sigma=1}^{s} [\hat{\psi}^{k\prime}(\mathbf{R}_\sigma) - \tilde{E}_k \hat{\psi}^k(\mathbf{R}_\sigma)]^2}{\sum_{\sigma=1}^{s} \hat{\psi}^k(\mathbf{R}_\sigma)^2},$$

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- full optimization of <u>all</u> parameters consists of a linear optimization nested in a non-linear one.

Numerical results: three-body case

	Kr_3		Ar_3		$\frac{1}{2}$-Ne_3	
D	E_1	ΔE_1	E_1	ΔE_1	E_1	ΔE_1
1	-1.872 548 547 6	-9$\times 10^{-1}$	-1.734 808 71	-8$\times 10^{-1}$	-0.895 584	-4$\times 10^{-1}$
2	-2.760 461 351 5	2$\times 10^{-10}$	-2.552 953 22	-1$\times 10^{-9}$	-1.302 484	-7$\times 10^{-7}$
3	-2.760 555 278 7	6$\times 10^{-10}$	-2.553 289 43	1$\times 10^{-8}$	-1.308 442	9$\times 10^{-6}$
4	-2.760 461 351 3	-5$\times 10^{-11}$	-2.552 953 22	-1$\times 10^{-9}$	-1.302 483	-2$\times 10^{-6}$
5	-2.760 179 569 8	-1$\times 10^{-9}$	-2.551 944 61	-2$\times 10^{-8}$	-1.284 627	-1$\times 10^{-5}$
6	-2.759 709 937 6	5$\times 10^{-10}$	-2.550 263 64	7$\times 10^{-9}$	-1.254 901	5$\times 10^{-6}$

Ground state energies E_1 (with errors in the last significant digit) and deviations from quadratic fits ΔE_1 for Kr_3, Ar_3 and $\frac{1}{2}$-Ne_3 in dimensions $D = 1$ through $D = 6$.

Numerical results: four-body case

D	E_1	ΔE_1
1	-2.625 622 56	-2$\times 10^{-0}$
2	-4.329 517 95	-8$\times 10^{-1}$
3	-5.118 146 05	-2$\times 10^{-9}$
4	-5.118 653 84	3$\times 10^{-9}$
5	-5.118 146 05	-2$\times 10^{-9}$
6	-5.116 622 70	1$\times 10^{-9}$

Ground state energies (with errors in the last significant digit) and deviations from quadratic fits ΔE_1 for Ar_4 in dimensions $D = 1$ through $D = 6$.

Numerical results: excited states Ar$_3$

k	$D=2$	$D=3$	$D=4$
2	-2.249 860 2	-2.250 185 5	-2.249 860
3	-2.126 038 8	-2.126 361	-2.126 039
4	-1.996 153	-1.996 43	-1.996 153
5	-1.946 3	-1.946 7	-1.946 3

Comparison of the excited state energies E_k (with errors in the last significant digit) of Ar$_3$ in $D = 2, 3$ and 4 dimensions.

Numerical results: excited states Ar$_4$

k	$D = 3$	$D = 5$
2	-4.800 897 73	-4.800 897 75
3	-4.725 156 7	-4.725 156 6
4	-4.630 025	-4.630 025
5	-4.586 389	-4.586 384

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- Consider more general D-dimensional Schrödinger equation

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- Mass of each particle may be different.

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where

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$$a_{i;j} = \sum_{\alpha=1}^{D} \frac{\partial^2 r_{ij}}{\partial x_{\alpha i}^2} = \frac{D-1}{r_{ij}}$$

$$g_{i;jk} = \sum_{\alpha=1}^{D} \frac{\partial r_{ij}}{\partial x_{\alpha i}} \frac{\partial r_{ik}}{\partial x_{\alpha i}} = \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{ik}}{r_{ij} r_{ik}}$$

angle: no D dependence

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- Use

$$\mathbf{H}\psi = E\psi \rightarrow \mathbf{H}'\phi = E\phi$$

with

$$\psi = \chi\phi \quad \text{and} \quad \mathbf{H}' = \frac{1}{\chi}\mathbf{H}\chi$$

Exact results

Result for general χ special case of Eq. (3.8) of Ref. [3] [J. Avery, D. G. Goodson, and D. R. Herschbach, Theor. Chim. Acta **81**, 1 (1991)]

$$\mathbf{H}' = V - \sum_{i=1} \frac{1}{2m_i}(S_i + T_i + U_i)$$

with

$$S_i = \sum_{j,k\neq i} g_{i;jk} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}},$$

$$T_i = \sum_{j\neq i} \left(a_{i;j} + 2 \sum_{k\neq i} g_{i;jk} \chi^{-1} \frac{\partial \chi}{\partial r_{ik}} \right) \frac{\partial}{\partial r_{ij}},$$

and a “centrifugal” contribution to the effective potential

$$U_i = \sum_{j\neq i} a_{i;j} \chi^{-1} \frac{\partial \chi}{\partial r_{ij}} + \sum_{j,k\neq i} g_{i;jk} \chi^{-1} \frac{\partial^2 \chi}{\partial r_{ik} \partial r_{ik}}.$$

Exact results

- Define N matrices of order $N-1$

$$\hat{G}_i = (r_{ij} g_{i;jk} r_{ik})_{j,k \neq i},$$

the Grammian associated with the $N-1$ vectors $\mathbf{r}_{ij}$ with $j = 1, \ldots, i-1, i+1, \ldots, N$.

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- Linear differential operators T_i vanish for the choice

$$\chi = \omega^{(1-D)/4}.$$

Exact results

- Contributions to effective potential

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\begin{aligned}
U_i &= \frac{1}{8}[(N-1)^2-(N-D)^2]\sum_{j\neq i}\frac{1}{r_{ij}}\frac{\partial\log\omega}{\partial r_{ij}} \\
&= \frac{(N-1)^2-(N-D)^2}{16\omega^2}\sum_{j,k\neq i}\frac{\partial\omega}{\partial r_{ij}}g_{i;jk}\frac{\partial\omega}{\partial r_{ik}}.
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- Amplitude is symmetric in D about $D=N$.
- Schrödinger equation has the same energy eigenvalues in $D=N-1$ and $D=N+1$.
- Energy minimum at $D=N$. (Last sum is sum of squares because $g_{i;jk}$ is an inner product.)

Summary and discussion

- Transformed the Schrödinger equation for S-states of N-particle clusters in $D \geq N-1$ dimensions into equation in $\frac{1}{2}(N-1)N$ variables.

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- The same applies to the spectrum.
- Continuation unrelated to physical spectrum of N particle clusters for $D \leq N-1$.
- Fundamental problem with the work by Gonzalez and Leal[6]: $1/D$ expansion estimates of energy levels of Lennard-Jones clusters in $D = 3$ with $N = 3, 4, \ldots, 7$ and 13 obained by analytic continuation from large D.

References

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