Conical Intersections in H3 near the United Atom Limit

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Outline of Talk

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- Standard Configuration, Permutation of Atom Names
- Three Electron Spin-Wavefunctions
- Hamiltonian omitting nuclear repulsion energy
- Ground State Energy and Eigenspace, Permutation Symmetry
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- The Doubly Degenerate Linear Shape
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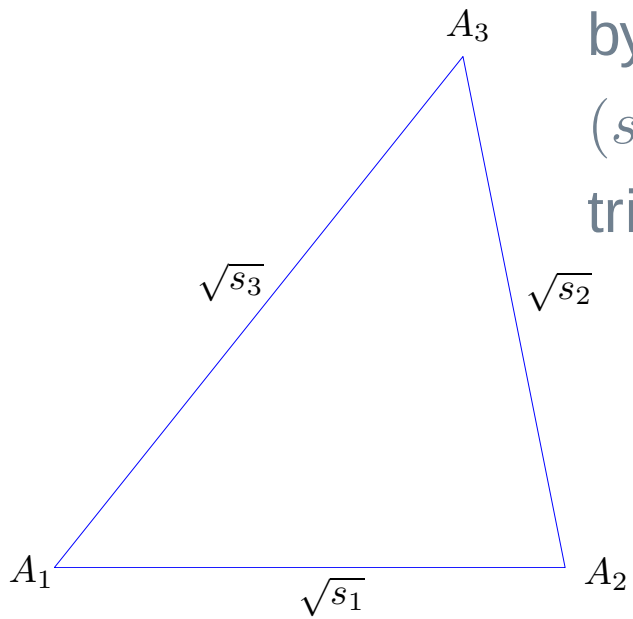
- References, Acknowledgment of Support

Nuclear Shape Space for H3



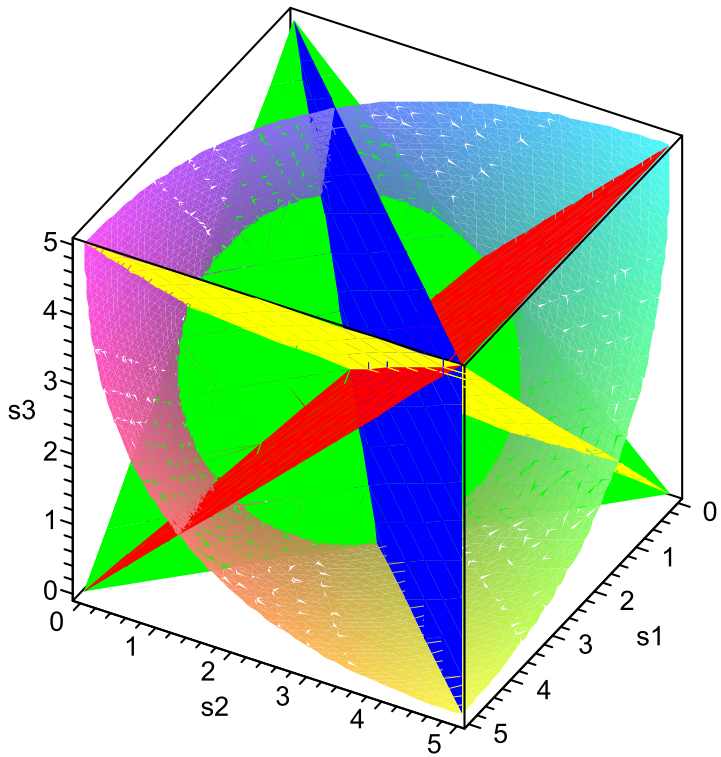
The shape of H3 is determined by three nonnegative parameters (s_1, s_2, s_3). These must satisfy the triangle inequalities:

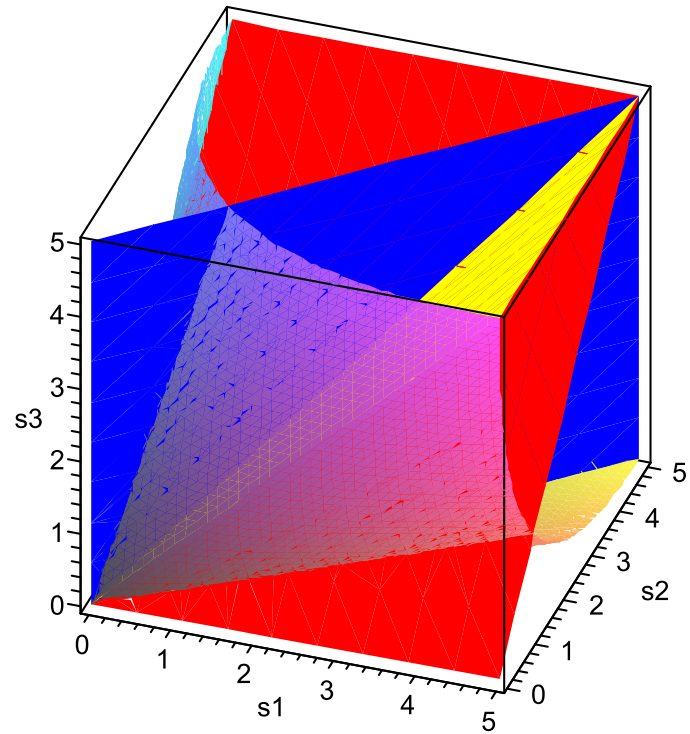
$$\sqrt{s_1} \leq \sqrt{s_2} + \sqrt{s_3}$$
$$\sqrt{s_2} \leq \sqrt{s_3} + \sqrt{s_1}$$
$$\sqrt{s_3} \leq \sqrt{s_1} + \sqrt{s_2}$$

These are all subsumed in the inequality for **the Cone**:

$$\sum_{i=1}^{3} [s_i - \tfrac{1}{3}(s_1 + s_2 + s_3)]^2 \leq \tfrac{1}{6}(s_1 + s_2 + s_3)^2.$$

Nuclear Shape Space for H3





Standard Configurations

There exist $\mathbb{R}^3$-valued functions $\mathbf{R}_i(s_1, s_2, s_3)$, $i = 1, 2, 3$ giving positions of atoms A_1, A_2, A_3 such that the z-coordinates are always zero, the center of mass is at the origin, and

$$\sqrt{s_i} = \|\mathbf{R}_i(s_1, s_2, s_3) - \mathbf{R}_j(s_1, s_2, s_3)\|,$$

$(i, j) = (1, 2), (2, 3), (3, 1)$. These functions are smooth in the interior of the Cone and extend uniquely and continuously to the boundary except at the diatomic points $s_3 = 0, s_1 = s_2 > 0$.

Permutations of Atom Names

For every permutation $(h(1), h(2), h(3))$ of $(1, 2, 3)$ (the edges of the triangle) there is an associated permutation $(h'(1), h'(2), h'(3))$ of $(1, 2, 3)$ (the atom names) and a 3×3 orthogonal matrix-valued function $T_h(s_1, s_2, s_3)$ such that

$$(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)(s_{h(1)}, s_{h(2)}, s_{h(3)}) = T_h(s_1, s_2, s_3)(\mathbf{R}_{h'(1)}, \mathbf{R}_{h'(2)}, \mathbf{R}_{h'(3)})(s_1, s_2, s_3).$$

$T_h(s_1, s_2, s_3)$ is smooth on the interior of the Cone, and fixes any vector parallel to the z-axis.

Three Electron Spin-Wavefunctions

Let $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ each range over $\mathbb{R}^3$ and k_1, k_2, k_3 each range over $\{0, 1\}$. $\mathbf{r}_i$ is the position of the ith electron and k_i is its spin in the z-direction, where $0 =$ spin up and $1 =$ spin down. Let $x_i = (\mathbf{r}_i, k_i)$, $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, $k = (k_1, k_2, k_3)$. Let $\mathcal{H}$ be the set of complex-valued functions $\psi(x_1, x_2, x_3) = \psi(\mathbf{r}, k)$ which are antisymmetric with respect to the interchange of any two x variables, and such that

$$\|\psi\|^2 = \sum_k \int_{\mathbb{R}^9} |\psi(\mathbf{r}, k)|^2 \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2 \, d^3\mathbf{r}_3 < \infty.$$

Applying Spin Operators

For each fixed $\mathbf{r}$ let $\psi(\mathbf{r}, \cdot)$ denote the column vector with 8 components $\psi(\mathbf{r}, k_1, k_2, k_3)$ numbered 0 to 7 in binary: $(k_1, k_2, k_3) = (000), (001), (010), \ldots, (111)$. Define the 8×8 spin matrices

$$S^2 = \frac{1}{4} \begin{pmatrix} 15 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 7 & 4 & 0 & 4 & 0 & 0 & 0 \\ 0 & 4 & 7 & 0 & 4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 7 & 0 & 4 & 4 & 0 \\ 0 & 4 & 4 & 0 & 7 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4 & 0 & 7 & 4 & 0 \\ 0 & 0 & 0 & 4 & 0 & 4 & 7 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 15 \end{pmatrix}, S_z = \frac{1}{2} \begin{pmatrix} 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3 \end{pmatrix}.$$

Thus $S^2\psi(\mathbf{r}, \cdot)$ and $S_z\psi(\mathbf{r}, \cdot)$ are 8 component column vectors, for each $\mathbf{r}$.

The Hamiltonian

If $\Delta_{\mathbf{r}_i}$ is the Laplacian acting in the variable $\mathbf{r}_i$ then define

$$H(s_1, s_2, s_3) = -\tfrac{1}{2}(\Delta_{\mathbf{r}_1} + \Delta_{\mathbf{r}_2} + \Delta_{\mathbf{r}_3}) - \sum_{i=1}^{3}\sum_{j=1}^{3} \frac{1}{\|\mathbf{R}_i(s_1, s_2, s_3) - \mathbf{r}_j\|} + \frac{1}{\|\mathbf{r}_1 - \mathbf{r}_2\|} + \frac{1}{\|\mathbf{r}_2 - \mathbf{r}_3\|} + \frac{1}{\|\mathbf{r}_3 - \mathbf{r}_1\|}.$$

The nuclear repulsion term $\sum_{i=1}^{3} \frac{1}{\sqrt{s_i}}$ is omitted.

Ground State Energy, Eigenspace

Define the **Ground State Energy** $E_0(s_1, s_2, s_3)$ to be

$$\min_{\psi \in \mathcal{H}, \|\psi\|=1} \sum_k \int_{\mathbb{R}^9} \psi(\mathbf{r}, k)^\dagger [H(s_1, s_2, s_3)\psi](\mathbf{r}, k)\, d^9\mathbf{r}.$$

Define the **Ground State Eigenspace** $\mathcal{F}(s_1, s_2, s_3)$ to be the set of all $\psi \in \mathcal{H}$ such that

$$[H(s_1, s_2, s_3)\psi](\mathbf{r}, k) = E_0(s_1, s_2, s_3)\psi(\mathbf{r}, k),$$

$$S_z\psi(\mathbf{r}, \cdot) = \tfrac{1}{2}\psi(\mathbf{r}, \cdot).$$

All $\psi \in \mathcal{F}(s_1, s_2, s_3)$ satisfy $S^2\psi(\mathbf{r}, \cdot) = \tfrac{3}{4}\psi(\mathbf{r}, \cdot)$.

Permutation Symmetry

If $(h(1), h(2), h(3))$ is a permutation of $(1, 2, 3)$ and $\psi \in \mathcal{F}(s_1, s_2, s_3)$ then define $(\mathcal{T}_h\psi)(\mathbf{r}, k) = \psi(T_h(s_1, s_2, s_3)^{-1}\mathbf{r}, k)$. It follows that $\mathcal{T}_h \colon \mathcal{F}(s_1, s_2, s_3) \to \mathcal{F}(s_{h(1)}, s_{h(2)}, s_{h(3)})$ is a linear isomorphism; furthermore $E_0(s_1, s_2, s_3) = E_0(s_{h(1)}, s_{h(2)}, s_{h(3)})$. Let U_n denote the set of all points (s_1, s_2, s_3) in the Cone such that $\mathcal{F}(s_1, s_2, s_3)$ has dimension n. Each set U_i is invariant with respect to permutation symmetry. $E_0(s_1, s_2, s_3)$ is continuous on the Cone and continuously differentiable on U_1, which is a relatively open and dense subset of the Cone.

Conical Intersections

We will say a **Conical Intersection** (CI) occurs at a point (s_1, s_2, s_3) of the Cone if $(s_1, s_2, s_3) \notin U_1$. CIs have long been known to occur at certain equilateral triangles, such as those with $s_1 = s_2 = s_3 \geq 1a_0^2$, which are in U_2. That U_2 should be a one parameter family has long been understood in terms of the eigenvalue crossings of 2×2 Hermitian matrices with certain constraints imposed by symmetry. But CIs have been observed in many non symmetric situations, which are difficult to rationalize. It makes sense to study all CIs in H3.

The Li Atom Limit

The point $(s_1, s_2, s_3) = (0, 0, 0)$ corresponds to a Lithium atom, and this point is in U_1. The points of the Cone near this vertex have very large physical energy, and so have not received much study. If all equilateral triangles were in U_2 then one could choose an orthonormal basis $\{\psi_1(s_1), \psi_2(s_1)\}$ of $\mathcal{F}(s_1, s_1, s_1)$ such that $\lim_{s_1 \to 0^+} \psi_1(s_1)$ spans $\mathcal{F}(0, 0, 0)$. But then $\psi_2(s_1)$ could not converge as $s_1 \to 0^+$ without a contradiction. Thus we expect very small equilateral triangles to be in U_1.

Bundle, Connection, Holonomy

If one attaches the one dimensional vector space $\mathcal{F}(s_1, s_2, s_3)$ to each point $(s_1, s_2, s_3) \in U_1$ one obtains what mathematicians call a **Line Bundle**. Since $\mathcal{F}(s_1, s_2, s_3) \subset \mathcal{H}$ for all $(s_1, s_2, s_3) \in U_1$ there is a natural **Connection** in this bundle: over any differentiable path $s(t) \in U_1$ a one parameter family $\psi(t) \in \mathcal{F}(s(t))$ is a **parallel vector field** if $\frac{d}{dt}\psi(t)$ is perpendicular to $\mathcal{F}(s(t))$ in $\mathcal{H}$ for each t. If $s(0) = s(1)$ and $\psi(t)$ is parallel over $s(t)$ then $\psi(1)$ is a constant multiple of $\psi(0)$; this numerical factor is called the **Holonomy** of the closed loop $s(t), 0 \leq t \leq 1$. It is independent of $\psi(t)$.

The Equilateral Triangle in U_3

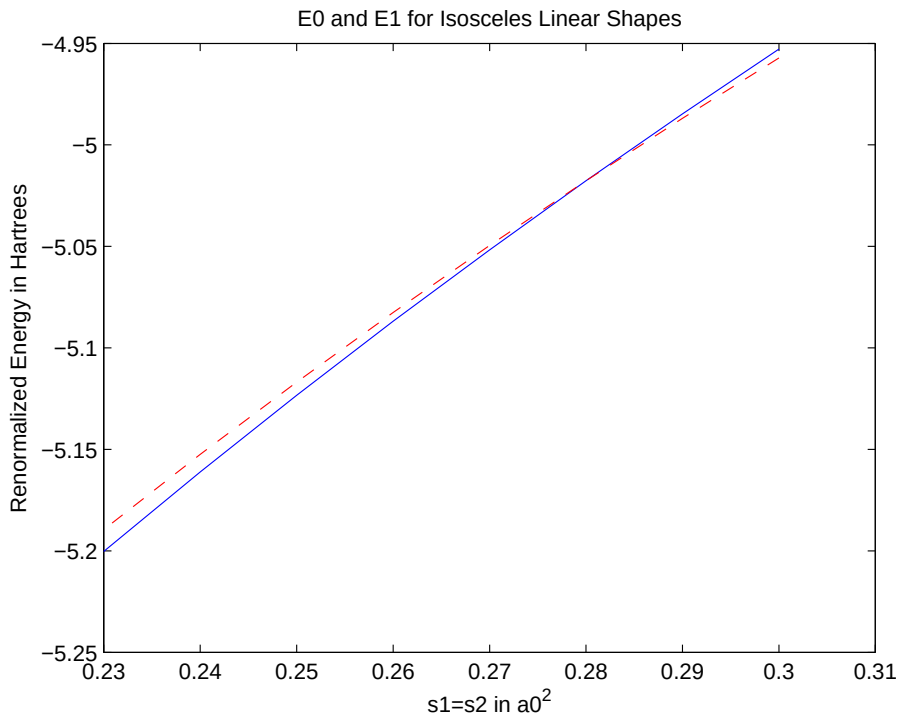
Computational studies of Mielke *et al* found an equilateral triangle with $s_1 = s_2 = s_3 = 0.88a_0^2$ that is in U_3. Those with $s_1 > 0.88a_0^2$ are in U_2. Those with $s_1 < 0.88a_0^2$ (that could be computed) are in U_1. The holonomy of a closed curve in U_1 stays constant as this curve is continuously deformed. The holonomy of a stationary curve (stays at a single point) is 1. The holonomy of a closed curve around the central axis of the cone, if $s_1 \geq 1$ is -1. Hence such curves cannot be deformed to stationary curves staying in U_1 throughout the deformation.

Isosceles Triangles in U_2

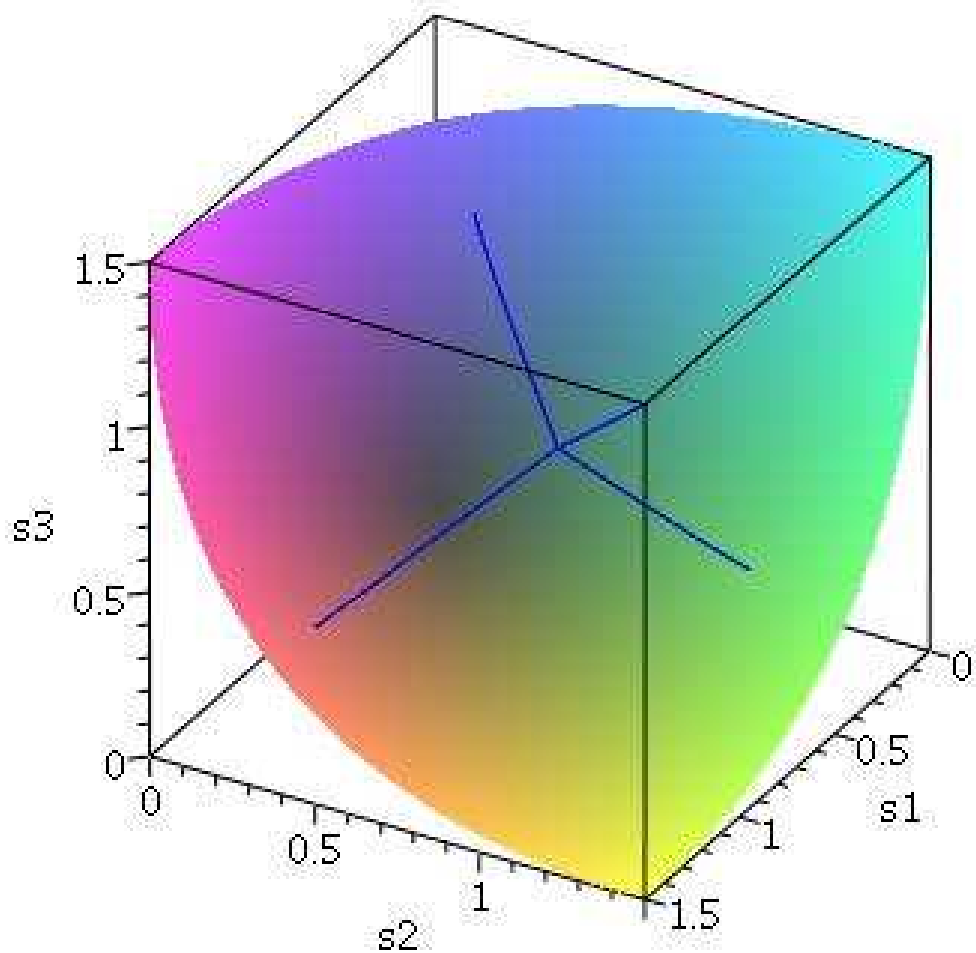
Thus we expect another (at least one) one parameter family of CIs emanating from the point in U_3. If no seam departs from the point in U_3 in one of the three planes of isosceles triangles then by symmetry there are $6m$ seams emanating from the point in U_3. By continuously deforming the closed loop around the central axis seam, whose holonomy is -1, we obtain a concatenation of $6m$ loops around each of the $6m$ seams, leading to the contradiction $-1 \neq (-1)^{6m}$. Thus we expect and observe an emerging seam of isosceles triangles.

Isosceles Linear Shape in U_2

Only three seams of isoceles triangles in U_2 are observed to emanate from the point in U_3, and each of these ends at the boundary of the Cone on a linear isosceles shape with $s_1 = s_2 = 0.28a_0^2$, $s_3 = 1.12a_0^2$ (or one of its permutations).



CI Seams in H3



Questions for Future Study

In order to better understand the reasons why CIs occur we hope to study the different electron distributions and spin couplings for the ground state wavefunction at points surrounding the CI points. The transition from the molecular pattern (electrons largely between nuclei) and the atomic pattern (electrons surround the nuclear region) can happen apart from or together with a CI. We would like to understand if this transition is contributing to the presence of CIs.

References, Acknowledgments

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