Supplemental Material: Dimer problem on a spherical surface

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A. Particle positions in $\vec{u}$ coordinates

The particle positions $\vec{r}_1$ and $\vec{r}_2$ can be expressed in terms of $\vec{n}_c$ and $\vec{n}_r$ as

$$\begin{aligned}\vec{r}_1 &= \vec{n}_c\cos(\theta/2) + \vec{n}_r\sin(\theta/2),\\ \vec{r}_2 &= \vec{n}_c\cos(\theta/2) - \vec{n}_r\sin(\theta/2),\end{aligned} \tag{A.1}$$

where the geodesic center-of-mass and relative vectors are respectively given by $\vec{n}_c = (\sin\beta\cos\alpha, \sin\beta\sin\alpha, \cos\beta)^T$ and $\vec{n}_r = \cos\gamma\,\vec{a} + \sin\gamma\,\vec{b}$. In particular, see Fig. 1, $\vec{a} = (-\cos\beta\cos\alpha, -\cos\beta\sin\alpha, \sin\beta)^T$ is the tangent vector to the center of mass directed along the great circle passing by the north pole, while $\vec{b} = (\sin\alpha, -\cos\alpha, 0)^T$ is the tangent vector to the center of mass directed along the circle parallel to the equator. Given the above relations, Eq. (A.1) represents the particles positions in terms of the angles $\vec{u}$.

The body-fixed frame is built on the basis vectors $\vec{n}_r$, $\vec{n}_c\times\vec{n}_r$, and $\vec{n}_c$, which define the x', y', and z' axes, respectively. The transition from the space-fixed to body-fixed frame is carried out with the help of the rotation matrix $\mathcal{R} = (\vec{n}_r, \vec{n}_c\times\vec{n}_r, \vec{n}_c)$ such that any vector $\vec{r}\,' = (x', y', z')^T$ defined in the body-fixed frame corresponds to $\vec{r} = \mathcal{R}\,\vec{r}\,'$ in the laboratory frame. For instance, the particles coordinates correspond to $\vec{r_1}\,' = (\sin(\theta/2), 0, \cos(\theta/2))^T$ and $\vec{r_2}\,' = (-\sin(\theta/2), 0, \cos(\theta/2))^T$.

B. Kinetic energy in $\vec{u}$ coordinates

The kinetic energy operator can be expressed in terms of the angles $\vec{u} = (\alpha, \beta, \gamma, \theta)$ by calculating the Laplace-Beltrami operator

$$\hat{T} = -\frac{1}{2}\frac{1}{\sqrt{g}}\partial_i(\sqrt{g}g^{ij}\partial_j), \tag{A.2}$$

where $\partial_i = \partial/\partial u^i$, $g = \det(g_{ij})$, and g^{ij} is the inverse of the metric tensor g_{ij}, defined through the line element squared ds^2 as $ds^2 = (d\vec{r}_1)^2 + (d\vec{r}_2)^2 = g_{ij}\,du^i du^j$. Thus, by differentiating the coordinates at Eq. (A.1) in terms of the angles $\vec{u}$, we obtain the metric tensor

$$g_{ij} = \begin{bmatrix} h_{ij} & \vec{0} \\ \vec{0} & 1/2 \end{bmatrix}, \tag{A.3}$$

with $g = \sin^2\beta\sin^2\theta$, and where the symmetric 3×3 tensor h has components

$$\begin{aligned}
h_{11} =& 2\sin^2\beta[\cos^2\gamma + \cos^2(\theta/2)\sin^2\gamma - \sin^2(\theta/2)\cos(2\gamma)] + \\
& 2\sin^2(\theta/2)\cos^2\beta,\\
h_{12} =& 2\sin^2(\theta/2)\sin\beta\sin\gamma\cos\gamma,\\
h_{13} =& 2\sin^2(\theta/2)\cos\beta,\\
h_{22} =& 2\sin^2\gamma + 2\cos^2(\theta/2)\cos^2\gamma + 2\sin^2(\theta/2)\cos(2\gamma),\\
h_{23} =& 0,\\
h_{33} =& 2\sin^2(\theta/2).
\end{aligned} \tag{A.4}$$

We calculate Eq. (A.2) explicitly and obtain the kinetic energy operator presented in the main text $\hat{T} = (\hat{J}^2_{x'}/I_{x'} + \hat{J}^2_{y'}/I_{y'} + \hat{J}^2_{z'}/I_{z'})/2 + \hat{L}^2_\theta$, whose angular momentum components are defined as

$$\begin{aligned}
\hat{J}_{x'} &= i\left(\frac{\cos\gamma}{\sin\beta}\partial_\alpha - \sin\gamma\partial_\beta - \cot\beta\cos\gamma\partial_\gamma\right),\\
\hat{J}_{y'} &= i\left(-\frac{\sin\gamma}{\sin\beta}\partial_\alpha - \cos\gamma\partial_\beta + \cot\beta\sin\gamma\partial_\gamma\right),\\
\hat{J}_{z'} &= -i\partial_\gamma,
\end{aligned} \tag{A.5}$$

in the molecular frame.

For completeness, we report the orthogonality relation of the Wigner-D functions used in the main text for projecting the Schrödinger equation [1]

$$\begin{aligned}
&\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta\sin\beta \int_0^{2\pi} d\gamma D^{j'*}_{m'l'}(\alpha,\beta,\gamma)D^{j}_{ml}(\alpha,\beta,\gamma)\\
&= \frac{8\pi^2}{2j+1}\delta_{jj'}\delta_{mm'}\delta_{ll'}.
\end{aligned}$$

C. Derivation of Eq. (8)

In this appendix we discuss the case $j = m \gg 1$. Let us write the two-body wave function in the form $\Psi(\theta_1, \phi_1, \theta_2, \phi_2) = \chi(y_1, y_2, x)e^{ij\phi_c}$, where $y_\sigma = \theta_\sigma - \pi/2$ is the deviation from the equator, $x = \phi_1 - \phi_2$, $\phi_c = (\phi_1 + \phi_2)/2$, and j is large integer, even or odd. The Schrödinger equation without interaction (1) in these co-

ordinates becomes

$$\sum_{\sigma=1,2}\left[-\frac{1}{2}\frac{\partial^2}{\partial y_\sigma^2}+\frac{\tan y_\sigma}{2}\frac{\partial}{\partial y_\sigma}+\frac{1}{\cos^2 y_\sigma}\left(\frac{j^2}{8}-\frac{1}{2}\frac{\partial^2}{\partial x^2}\right)\right]\chi - \frac{j}{2}\left(\frac{1}{\cos^2 y_1}-\frac{1}{\cos^2 y_2}\right) i\frac{\partial}{\partial x}\chi = E\chi. \tag{A.6}$$

The interaction is taken into account via a Bethe-Peierls boundary condition at $\{x, y_1 - y_2\} = \mathbf{0}$. Let us assume (and a posteriori verify) that $y_\sigma \sim 1/\sqrt{j}$, $\partial/\partial y_\sigma \sim \sqrt{j}$, and that $\partial/\partial x$ is at most of order $\sqrt{j}$. Then, keeping only terms $\sim j^2\chi$ and $j\chi$ Eq. (A.6) reduces to

$$\left(-\frac{1}{4}\frac{\partial^2}{\partial Y^2}+\frac{j^2}{4}Y^2-\frac{\partial^2}{\partial y^2}+\frac{j^2}{16}y^2-\frac{\partial^2}{\partial x^2}+\frac{j^2}{4}\right)\chi = E\chi \tag{A.7}$$

with $y = y_1 - y_2$ and $Y = (y_1 + y_2)/2$. We thus arrive at the problem of two atoms of unit mass trapped in the y direction by a harmonic potential with frequency $j/2$. As we mention in the main text this confinement arises from the expansion of the term $j^2/(8\cos^2 y_\sigma)$ in Eq. (A.6) in powers of y_σ. It reflects the centrifugal barrier felt by the atoms as they deviate from the equator trying to approach any of the poles.

Equation (A.7) is supplemented by the periodicity condition $\chi(Y, x, y) = (-1)^j\chi(Y, 2\pi+x, y)$ and by the Bethe-Peierls constraint on the asymptotic behavior of the wave function $\chi(Y, x \to 0, y \to 0) \propto \ln[(x^2 + y^2)/a^2]$. The center-of-mass motion separates from the relative one: $\chi(Y, x, y) = e^{-jY^2/2}\tilde{\chi}(x, y)$. The relative wave function $\tilde{\chi}$ can be written in the form of the Green function of a harmonic oscillator [2] adapted to satisfy the periodicity condition

$$\tilde{\chi}(x,y) = \sum_{n=-\infty}^{\infty}(-1)^{jn}\int_0^\infty \frac{e^{-y^2\frac{\coth\tau}{4l_\perp^2}+q^2l_\perp^2\tau+\frac{\tau}{2}-\frac{(x+2\pi n)^2}{4\tau l_\perp^2}}}{4\pi\sqrt{\tau\sinh\tau}}d\tau, \tag{A.8}$$

where $l_\perp = \sqrt{2/j}$ is the oscillator length. The total energy $E = j^2/4 + j/2 + q^2$ decomposes into the kinetic energy of the center-of-mass motion along the equator ($j^2/4$), the center-of-mass zero-point energy along y ($j/4$), the relative zero-point energy ($j/4$), and the energy of the relative motion along x which we denote by q^2.

We now establish the relation between q^2 and a applying the Bethe-Peierls constraint, which is sufficient to write as $\tilde{\chi}(x, 0) \propto \ln(x/a)$. Adding and subtracting the logarithmically diverging part from Eq. (A.8) and then setting $x = 0$ in the nondiverging terms gives

$$\tilde{\chi}(x,0) = F_1(x) + F_2 + F_3 + o(x^0), \tag{A.9}$$

where

$$F_1(x) = \int_0^\infty e^{q^2l_\perp^2\tau - x^2/(4\tau l_\perp^2)}\frac{d\tau}{4\pi\tau} = K_0(\sqrt{-q^2l_\perp^2}\,x)/(2\pi) = -\ln(\sqrt{-q^2x^2}e^{\gamma_E}/2)/(2\pi) + o(x^0), \tag{A.10}$$

$$F_2 = \int_0^\infty e^{q^2l_\perp^2\tau}\left(\sqrt{\tau/\sinh\tau}e^{\tau/2}-1\right)\frac{d\tau}{4\pi\tau}, \tag{A.11}$$

and

$$F_3 = \sum_{n=-\infty, n\neq 0}^{\infty}(-1)^{jn}\int_0^\infty \frac{e^{q^2l_\perp^2\tau+\frac{\tau}{2}-\frac{(2\pi n)^2}{4\tau l_\perp^2}}}{4\pi\sqrt{\tau\sinh\tau}}d\tau \approx \frac{1}{[e^{2\pi\sqrt{-q^2}}-(-1)^j]\sqrt{-2\pi q^2 l_\perp^2}}. \tag{A.12}$$

In Eq. (A.12) we use the fact that the main contribution to the integral comes from $\tau \sim 1/l_\perp^2 \gg 1$. Then, approximating $\sinh\tau \approx e^\tau/2$ the integral and the sum in Eq. (A.12) can be calculated analytically. The relation between q and a is obtained by noting that according to the Bethe-Peierls condition Eq. (A.9) should behave as $-\ln(x/a)/(2\pi)$ at small x. In this manner we obtain

$$\int_0^\infty e^{q^2l_\perp^2\tau}\left(\sqrt{\tau/\sinh\tau}e^{\tau/2}-1\right)\frac{d\tau}{4\pi\tau} + \frac{1}{[e^{2\pi\sqrt{-q^2}}-(-1)^j]\sqrt{-2\pi q^2l_\perp^2}} = \frac{1}{2\pi}\ln\frac{\sqrt{-q^2}ae^{\gamma_E}}{2}. \tag{A.13}$$

We now discuss validity of Eq. (A.13). When the distance between the two atoms is larger than $l_\perp$, i.e., when $|x + 2\pi n| \gtrsim 1/\sqrt{j}$ (for any integer n), the wave function χ behaves as

$$\chi(Y, x, y) \propto e^{-jY^2/2 - jy^2/8}\sum_n(-1)^{nj}e^{-\sqrt{-q^2}|x+2\pi n|}. \tag{A.14}$$

We derive Eq. (A.14) from Eq. (A.8) by using the approximations $\coth\tau \approx 1$ and $\sinh\tau \approx e^\tau/2$ valid since typical τ are large. We see that the characteristic length scale for the variation of χ in the y direction is indeed $\sim 1/\sqrt{j}$ and the characteristic length scale in the x direction is $1/|q|$. This verifies that Eq. (A.7) is valid for $|q| \sim \partial/\partial x \lesssim \sqrt{j}$ as we initially assumed.

We remind that passing from Eq. (A.6) to Eq. (A.7) we kept only terms of order j^2 and j. Therefore, in principle, we should not allow $|q^2|$ to be smaller than j in order not to exceed the accuracy of the approximation. Under this condition the size of the dimer is smaller than the sphere radius and the exponentially small second term in the left-hand side of Eq. (A.13) can be neglected leading to Eq. (8) of the main text, for which we require $-q^2 \gg 1$.

However, considering the difference between Eqs. (A.7) and (A.6) as the perturbation and Eq. (A.14) as the unperturbed solution to the harmonic problem Eq. (A.7), one can show that the first-order and higher-order energy shifts are of order $\max\{q^2, 1\}/j$. We can thus claim that Eq. (A.13) also makes sense for $q^2 \sim 1$ and can describe the whole crossover from the isotropic molecule ($|q| \sim \sqrt{j}$) to the noninteracting limit $a \to \infty$ where it correctly reproduces Eqs. (7) predicting $q^2 = 0$ for even j and $q^2 = 1/4$ for odd j. To solve Eq. (A.13) for positive q^2 we use analytical continuation.

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