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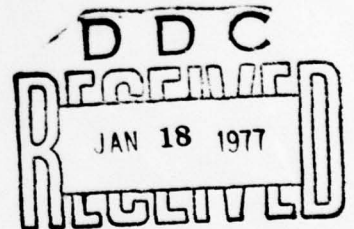
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ABSTRACT

The natural orbitals are derived for a
pair of identical coupled harmonic oscillators in
their ground state.

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COUPLED-OSCILLATOR NATURAL ORBITALS

Peter D. Robinson

Examples of natural orbitals in closed form seem rare enough [1] to justify this note, in which such orbitals are exhibited for coupled oscillators.

Let $\{\theta_n(\alpha, x)\}$ denote the complete set of orthonormal eigenfunctions of the oscillator Hamiltonian

$$h(\alpha, x) = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \alpha^4 x^2, \quad \alpha > 0, \quad -\infty < x < \infty, \quad (1)$$

corresponding to the eigenvalues $(n + \frac{1}{2})\alpha^2$. Specifically

$$\theta_n(\alpha, x) = \left[\frac{\alpha}{\pi^{\frac{1}{2}} 2^n n!} \right]^{\frac{1}{2}} H_n(\alpha x) \exp(-\frac{1}{2} \alpha^2 x^2), \quad n = 0, 1, 2, \dots, \quad (2)$$

where the Hermite polynomials $H_n(\alpha x)$ are orthogonalized with respect to a weight factor [2] $\exp(-\alpha^2 x^2)$. Consider now the identical coupled oscillators described by the Hamiltonian

$$H = -\frac{1}{2} \frac{d^2}{dx_1^2} - \frac{1}{2} \frac{d^2}{dx_2^2} + \frac{1}{2} a^4 (x_1^2 + x_2^2) - \frac{1}{4} (a^4 - b^4) (x_1 - x_2)^2, \quad (3)$$

$$a > b > 0, \quad -\infty < x_1 < \infty, \quad -\infty < x_2 < \infty.$$

In terms of the coordinates

$$y_1 = \frac{1}{\sqrt{2}} (x_1 + x_2), \quad y_2 = \frac{1}{\sqrt{2}} (x_1 - x_2), \quad (4)$$

the Hamiltonian (3) takes the separable form

$$H = h(a, y_1) + h(b, y_2) . \quad (5)$$

The ground-state wave-function thus has a space part

$$\begin{aligned} \psi(x_1, x_2) &= \theta_0(a, y_1) \theta_0(b, y_2) = \left(\frac{ab}{\pi} \right)^{\frac{1}{2}} \exp\left(-\frac{1}{2} a^2 y_1^2 - \frac{1}{2} b^2 y_2^2\right) \\ &= \left(\frac{ab}{\pi} \right)^{\frac{1}{2}} \exp\left\{-\frac{1}{4} (a^2 + b^2)(x_1^2 + x_2^2) - \frac{1}{2} (a^2 - b^2)x_1 x_2\right\} , \end{aligned} \quad (6)$$

which is the eigenfunction of the operator (5) corresponding to the eigenvalue $\frac{1}{2} (a^2 + b^2)$.

This function $\psi(x_1, x_2)$ is symmetric in x_1 and x_2 , and is normalized so that

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^2 dx_1 dx_2 = 1 . \quad (7)$$

Accordingly, $\psi(x_1, x_2)$ is the Hilbert-Schmidt-type kernel of a compact, self-adjoint integral operator on the real Hilbert space $L_2(-\infty, \infty)$. Standard integral equation theory [3] tells us that this operator has a complete orthonormal set of eigenvectors $\{\phi_n\}$ defined by

$$\int_{-\infty}^{\infty} \psi(x_1, x_2) \phi_n(x_2) dx_2 = \lambda_n \phi_n(x_1), \quad n = 0, 1, 2, \dots , \quad (8)$$

with the eigenvalues λ_n accumulating at zero. Further, the expansion

$$\frac{1}{2} \gamma(x_1, x_2) = \int_{-\infty}^{\infty} \psi(x_1, s) \psi(x_2, s) ds = \sum_{n=0}^{\infty} \lambda_n^2 \phi_n(x_1) \phi_n(x_2) \quad (9)$$

is convergent for all x_1 and x_2 . The functions $\phi_n(x)$ are precisely the natural orbitals for $\psi(x_1, x_2)$, and (9) gives the expansion for the first-order density matrix $\gamma(x_1, x_2)$. The "occupation numbers" λ_n^2 must sum to unity, from (7) and (9). The expansion for $\psi(x_1, x_2)$ itself, namely

$$\psi(x_1, x_2) \sim \sum_{n=0}^{\infty} \lambda_n \phi_n(x_1) \phi_n(x_2), \quad (10)$$

must also be convergent, at least in the L_2 norm sense.

In the case of the function given in (6), the expansion (10) can be found directly, and is convergent for all x_1 and x_2 . Mehler's formula [2] states that

$$\exp\left\{-\frac{z^2}{1-z^2}(t_1^2 + t_2^2) + \frac{2z}{1-z^2}t_1t_2\right\} = (1-z^2)^{\frac{1}{2}} \sum_{n=0}^{\infty} \frac{z^n}{2^n n!} H_n(t_1) H_n(t_2),$$

$$-1 < z < 1, \quad -\infty < t_1 < \infty, \quad -\infty < t_2 < \infty. \quad (11)$$

Setting $t_1 = \alpha x_1$, $t_2 = \alpha x_2$ and multiplying through by $\exp\{-\frac{1}{2}\alpha^2(x_1^2 + x_2^2)\}$, we obtain from (2):

$$\frac{\alpha}{\pi^{\frac{1}{2}}} \exp\left\{-\left(\frac{1+z^2}{1-z^2}\right) \frac{\alpha^2}{2}(x_1^2 + x_2^2) + 2 \frac{\alpha^2 z}{1-z^2} x_1 x_2\right\} = (1-z^2)^{\frac{1}{2}} \sum_{n=0}^{\infty} z^n \theta_n(\alpha, x_1) \theta_n(\alpha, x_2). \quad (12)$$

With the choices

$$\alpha = (ab)^{\frac{1}{2}}, \quad z = -\frac{a-b}{a+b} \quad (13)$$

the left-hand side of (12) becomes $\psi(x_1, x_2)$ as given in (6). Thus

$$\psi(x_1, x_2) = \sum_{n=0}^{\infty} \left\{ \frac{2\sqrt{ab}}{a+b} (-1)^n \left(\frac{a-b}{a+b} \right)^n \right\} \theta_n(\sqrt{ab}, x_1) \theta_n(\sqrt{ab}, x_2), \quad (14)$$

so that for the ground-state of the coupled oscillators we have the natural orbitals

$$\phi_n(x) = \theta_n(\sqrt{ab}, x) = \left[\frac{\sqrt{ab}}{\pi^{\frac{1}{2}} 2^n n!} \right]^{\frac{1}{2}} H_n(\sqrt{ab} x) \exp(-\frac{1}{2} ab x^2), \quad (15)$$

and corresponding eigenvalues

$$\lambda_n = \frac{2\sqrt{ab}}{a+b} (-1)^n \left(\frac{a-b}{a+b} \right)^n. \quad (16)$$

The orbitals (15), and the occupation numbers λ_n^2 , can also be obtained by working from the expression for $\frac{1}{2} \gamma(x_1, x_2)$, which is

$$\frac{1}{2} \gamma(x_1, x_2) = ab \left[\frac{\pi}{2} (a^2 + b^2) \right]^{-\frac{1}{2}} \exp \left\{ -\frac{(a^4 + b^4 + 6a^2 b^2)}{8(a^2 + b^2)} (x_1^2 + x_2^2) + \frac{(a^2 - b^2)^2}{4(a^2 + b^2)} x_1 x_2 \right\}. \quad (17)$$

Extension to three-dimensional oscillators, for which Davidson [1] has discussed the first-order density matrix, is straightforward.

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3. R. Courant and D. Hilbert, *Methods of Mathematical Physics*, I, (Interscience) 1953.

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