Exact phase space functional for two-body systems

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(Dated: 21 November 2010)

The determination of the two-body density functional from its one-body density is achieved for Moshinsky's harmonium model, using a phase-space formulation, thereby resolving its phase dilemma. The corresponding sign rules can equivalently be obtained by minimizing the ground-state energy.

I. INTRODUCTION

The harmonium model originally proposed by Moshinsky[1] has earned its spurs as a simple analogue to a two-electron atom, helpful to illustrate the main ideas of reduced density matrix and correlation energy theory in an exactly solvable context. The model consists of two spin-$\frac{1}{2}$ fermions trapped in a harmonic potential and repelling each other with a Hooke's law force, as well. Chapter 2 of the book by Davidson[2] describes its ground state in the standard wave function formalism, as well as the reduced density matrix and the pair distribution, exhibiting correlation.

A one-dimensional version of the model was put to work by Neal[3] in the hope of finding an exact universal density functional of the Hohenberg–Kohn–Sham type.[4] This proves illusory; but the computations by Schindlmayr in his very pedagogical rejoinder[5] make it clear that Neal's harmonium scheme supports successful approximations for confining potentials. More recently, the harmonium model has proved its worth in suggesting approximate general forms of 1-density matrices[6] and Ansätze for correlation energy density.[7]

The advantage of the harmonium model is that the required computations can be analytically performed. However, despite this solvable character, several pertinent functionals have not been exploited so far. It is well known that possession of the 1-body matrix ρ_1 for an N-electronic system does not allow effective inference of the corresponding 2-body ma-

trix ρ_2, which would trivialize the energy functional in quantum chemistry. It is natural to diagonalize ρ_1 and seek to expand ρ_2 in terms of eigenfunctions f_j of ρ_1 ("natural orbitals") and its eigenvalues $0 \leq n_j \leq 1$ ("occupation numbers"), with $\sum_j n_j = 1$. Over the years, starting with the work by Müller, approximate functionals based on this spectral analysis of ρ_1 have been suggested and tried with various results.

Two-electron atoms constitute the exception to our ignorance. In this article we focus on the *exact* Shull–Löwdin–Kutzelnigg (SLK) functional for the ground state of such atoms in terms of natural orbitals.[2,8,9] Work by those authors in the late fifties and early sixties established that, for a reduced 1-density of the kind

$$\rho_1(\boldsymbol{x}, \boldsymbol{x}') = \frac{1}{2}\left(\uparrow_1\uparrow_{1'} + \downarrow_1\downarrow_{1'}\right)\rho_1(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{2}\left(\uparrow_1\uparrow_{1'} + \downarrow_1\downarrow_{1'}\right)\sum_j n_j f_j(\boldsymbol{r}) f_j^*(\boldsymbol{r}'),$$

the corresponding 2-density matrix is given by the form

$$\rho_2(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_1', \boldsymbol{x}_2') = \frac{1}{2}\left(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\right)\left(\uparrow_{1'}\downarrow_{2'} - \downarrow_{1'}\uparrow_{2'}\right) \tag{1}$$

$$\times \left(f_1(\boldsymbol{r}_1) \ f_2(\boldsymbol{r}_1) \ f_3(\boldsymbol{r}_1) \ \cdots\right) \begin{pmatrix} c_1 & & & \\ & c_2 & & \\ & & c_3 & \\ & & & \ddots \end{pmatrix} \begin{pmatrix} f_1(\boldsymbol{r}_2) \\ f_2(\boldsymbol{r}_2) \\ f_3(\boldsymbol{r}_2) \\ \vdots \end{pmatrix}$$

$$\times \left(f_1^*(\boldsymbol{r}_1') \ f_2^*(\boldsymbol{r}_1') \ f_3^*(\boldsymbol{r}_1') \ \cdots\right) \begin{pmatrix} c_1^* & & & \\ & c_2^* & & \\ & & c_3^* & \\ & & & \ddots \end{pmatrix} \begin{pmatrix} f_1^*(\boldsymbol{r}_2') \\ f_2^*(\boldsymbol{r}_1') \\ f_3^*(\boldsymbol{r}_2') \\ \vdots \end{pmatrix}.$$

Alas, the SLK recipe, although exact, is underdetermined: of the c_j we only know that $|c_j|^2 = n_j$. This is a "phase dilemma" of density functional theory. We work here only with states described by real wavefunctions —still leaving us with an infinite number of signs to account for.

Notwithstanding its venerable age, formula (1) apparently has never been verified exactly. A theorem without an example is a sorry thing. Of course, numerical computations tend to confirm the SLK theorem; but one should not forget that they tell us about the approximations (nearly always from a Hartree–Fock starting point), rather than the true solution. We verify the SLK method for harmonium in full detail, including the energy functional, in the

following three sections. Along the way, we solve the sign conundrum for the model. Our methods are elementary, asking familiarity with little more than orthogonal polynomials at the level of Lebedev[10] or Andrews *et al.*[11]

Nevertheless, within the standard formalism it is not at all obvious how to go about the problem. We manage to sidestep difficulties by working with the Wigner quasiprobability on phase space instead. A recent quantum phase space view of harmonium, dealing with other matters, is given by Dahl.[12]

In the concluding Section 5 we very briefly discuss the new perspectives on correlation energy and approximate functionals for ρ_2 revealed by the treatment in this paper.

We follow Davidson's notation[2] as much as feasible. A good review on the Müller functional is found in Ref. 13. One may consult Refs. 14, 15 for popular variations on it.

II. THE SETUP

The Hamiltonian for harmonium in Hartree units is

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{k}{2}(r_1^2 + r_2^2) - \frac{\delta}{4}r_{12}^2. \tag{2}$$

Introduce extracule and intracule coordinates, respectively given by

$$\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/\sqrt{2}, \qquad \boldsymbol{r} = (\boldsymbol{r}_1 - \boldsymbol{r}_2)/\sqrt{2},$$

with conjugate momenta

$$\boldsymbol{P} = (\boldsymbol{p}_1 + \boldsymbol{p}_2)/\sqrt{2}, \qquad \boldsymbol{p} = (\boldsymbol{p}_1 - \boldsymbol{p}_2)/\sqrt{2}.$$

Therefore

$$H = H_R + H_r = \frac{P^2}{2} + \frac{\omega^2 R^2}{2} + \frac{p^2}{2} + \frac{\mu^2 r^2}{2}.$$

As advertised, our notation is that of Davidson[2] except that our δ is equal to twice his α, and we introduce the frequencies $\omega = \sqrt{k}$ and $\mu = \sqrt{k - \delta}$; assume $0 \leq \delta < k$ for both particles to remain in the potential well.

Since the spin factors are known, we concentrate on the spinless part of the quantum states henceforth. The spinless Wigner quasiprobability (normalized to one) corresponding to a (real) 2-particle wave function Ψ is given by

$$P_\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) = \frac{1}{\pi^6} \int \rho_2(\boldsymbol{r}_1 - \boldsymbol{z}_1, \boldsymbol{r}_2 - \boldsymbol{z}_2; \boldsymbol{r}_1 + \boldsymbol{z}_1, \boldsymbol{r}_2 + \boldsymbol{z}_2) \, e^{2i(\boldsymbol{p}_1 \cdot \boldsymbol{z}_1 + \boldsymbol{p}_2 \cdot \boldsymbol{z}_2)} \, d^3 z_1 \, d^3 z_2, \tag{3}$$

with $\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_1', \boldsymbol{r}_2') = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)\Psi(\boldsymbol{r}_1', \boldsymbol{r}_2')$. The definition extends to transition matrices $|\Phi\rangle\langle\Phi'|$ also:

$$P_{\Phi\Phi'}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) = \frac{1}{\pi^6} \int \Phi(\boldsymbol{r}_1 - \boldsymbol{z}_1, \boldsymbol{r}_2 - \boldsymbol{z}_2)\Phi'(\boldsymbol{r}_1 + \boldsymbol{z}_1, \boldsymbol{r}_2 + \boldsymbol{z}_2) \, e^{2i(\boldsymbol{p}_1 \cdot \boldsymbol{z}_1 + \boldsymbol{p}_2 \cdot \boldsymbol{z}_2)} \, d^3 z_1 \, d^3 z_2.$$

Fourier analysis easily provides the inverse formula to this, that we do not bother to write.

By use of (3) and the ground state wave function for harmonium, one can obtain the corresponding Wigner function, which factorizes into extracule and intracule parts:

$$P_{\mathrm{gs}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) = \frac{1}{\pi^6} \exp\left(-\frac{2H_R}{\omega}\right) \exp\left(-\frac{2H_r}{\mu}\right). \tag{4}$$

This is reached more efficiently and elegantly by the methods of phase space quantum mechanics.[16] One can now obtain ρ_2, given by the inverse formula of (3). The pairs density $\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_2)$ is recovered by integration over the momenta.

The reduced 1-body phase space (spinless) quasidensity for the ground state d_{gs} is obtained, as in the standard formalism, by integrating out one set of variables,

$$d_{\mathrm{gs}}(\boldsymbol{r}; \boldsymbol{p}) = \frac{2}{\pi^3} \left(\frac{4\omega\mu}{(\omega + \mu)^2}\right)^{3/2} e^{-2r^2\omega\mu/(\omega+\mu)} e^{-2p^2/(\omega+\mu)}. \tag{5}$$

We leave it as an exercise for the reader to recover Eq. (2–68) of Ref. 2 for $\rho_1(\boldsymbol{r}_1, \boldsymbol{r}_1')$ from this. The marginals of d_{gs} give the electronic density and momentum density.

It should be recognized that, while P_{gs} is a pure state, mathematically d_{gs} describes a mixed state. For Gaussians on phase space, such as P_{gs} and d_{gs} too, there are simple rules to determine whether they represent a pure state,[17] a mixed state,[18] or neither. Writing $\boldsymbol{q} = (\boldsymbol{r}_1, \boldsymbol{r}_2)$, $\boldsymbol{\pi} = (\boldsymbol{p}_1, \boldsymbol{p}_2)$, $\boldsymbol{u} = (\boldsymbol{q}, \boldsymbol{\pi})$, we find $P_{\mathrm{gs}}(\boldsymbol{u}) = \pi^{-6} e^{-\boldsymbol{u} \cdot F\boldsymbol{u}} = \pi^{-6} e^{-\boldsymbol{q} \cdot A\boldsymbol{q} - \boldsymbol{\pi} \cdot A^{-1}\boldsymbol{\pi}}$ where, amusingly,

$$A = \frac{1}{2}\begin{pmatrix} \omega + \mu & \omega - \mu \\ \omega - \mu & \omega + \mu \end{pmatrix}, \qquad A^{-1} = \frac{1}{2}\begin{pmatrix} \omega^{-1} + \mu^{-1} & \omega^{-1} - \mu^{-1} \\ \omega^{-1} - \mu^{-1} & \omega^{-1} + \mu^{-1} \end{pmatrix}. \tag{6}$$

We see that the matrix F corresponding to formula (4) is symmetric and symplectic, and therefore represents a pure state. This is not the case for d_{gs}. Thus recovering P_{gs} from knowledge of d_{gs} alone is akin to putting Humpty Dumpty together again!

III. COMPUTATION OF THE 2-BODY QUASIDENSITY

Since all the relevant quantities factorize, in this section we work in one dimension (instead of three) for notational simplicity. The real quadratic form in the exponent of d_{gs} must be

symplectically congruent to a diagonal one.[18] We perform the transformation

$$(Q, P) := \big((\omega\mu)^{1/4} r, (\omega\mu)^{-1/4} p\big); \quad \text{or, in shorthand,} \quad U = Su,$$

where now $u = (r, p)$. Here S being symplectic just means having determinant 1, which is evidently the case. Introducing as well the parameter $\lambda := 2\sqrt{\omega\mu}/(\omega+\mu)$, the 1-quasidensity takes the simple form

$$d_{\text{gs}}\big(u(U)\big) = \frac{\lambda}{\pi} e^{-\lambda U^2}.$$

We may also write $\lambda =: \tanh(\beta/2)$, so that

$$\beta = \log\frac{1+\lambda}{1-\lambda} = 2\log\frac{\sqrt{\omega}+\sqrt{\mu}}{\sqrt{\omega}-\sqrt{\mu}}, \quad \text{and} \quad \sinh(\beta/2) = \frac{\lambda}{\sqrt{1-\lambda^2}} = \frac{2\sqrt{\omega\mu}}{\omega-\mu}.$$

From the series formula, valid for $|t| < 1$,

$$\sum_{n=0}^{\infty} L_n(x)\, e^{-x/2}\, t^n = \frac{1}{(1-t)}\, e^{-x(1+t)/2(1-t)},$$

taking $t = -(1-\lambda)/(1+\lambda) = -e^{-\beta}$ and $x = 2U^2$, it follows that

$$\frac{\lambda}{\pi} e^{-\lambda U^2} = \frac{2}{\pi} \sinh\frac{\beta}{2} \sum_{r=0}^{\infty} (-1)^r L_r(2U^2)\, e^{-U^2} e^{-(2r+1)\beta/2}.$$

We recognize the basis of Wigner eigenfunctions on phase space standing for the oscillator states:[16]

$$f_{rr}(U) = \frac{1}{\pi}\, (-1)^r L_r(2U^2)\, e^{-U^2}.$$

Note the normalization $\int f_{rr}^2(Q,P)\, dU = (2\pi)^{-1}$. Consequently, we realize that d_{gs} is in thin disguise a *Gibbs state*,[18] with inverse temperature β:

$$d_{\text{gs}}(u) = d_{\text{gs}}(S^{-1}U) = 2\sinh\frac{\beta}{2} \sum_{r=0}^{\infty} e^{-(2r+1)\beta/2} f_{rr}(U). \tag{7}$$

Thus we have identified the natural orbitals in the U variables. Their occupation numbers are

$$n_r = 2\sinh\frac{\beta}{2} e^{-(2r+1)\beta/2} = \frac{4\sqrt{\omega\mu}}{\omega-\mu}\left(\frac{\sqrt{\omega}-\sqrt{\mu}}{\sqrt{\omega}+\sqrt{\mu}}\right)^{2r+1} = \frac{4\sqrt{\omega\mu}}{(\sqrt{\omega}+\sqrt{\mu})^2}\left(\frac{\sqrt{\omega}-\sqrt{\mu}}{\sqrt{\omega}+\sqrt{\mu}}\right)^{2r}. \tag{8}$$

Notice that $n_0 = 1 - e^{-\beta} = Z^{-1}(\beta)$, where Z is the partition function for the system; also $\sum_r n_r = (1 - e^{-\beta}) \sum_r e^{-r\beta} = 1$. These n_r have nice square roots:

$$\sqrt{n_r} = \frac{2(\omega\mu)^{1/4}}{\sqrt{\omega}+\sqrt{\mu}}\left(\frac{\sqrt{\omega}-\sqrt{\mu}}{\sqrt{\omega}+\sqrt{\mu}}\right)^r.$$

We prepare now to test the SLK functional. On phase space, formula (1) is replaced by

$$P_{2\,\text{SLK}}(u_1, u_2; \text{spin}) = \frac{1}{2}\big(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\big)\big(\uparrow_{1'}\downarrow_{2'} - \downarrow_{1'}\uparrow_{2'}\big)\sum_{r,s=0}^{\infty} c_r c_s\, f_{rs}(u_1) f_{rs}(u_2). \qquad (9)$$

The f_{rs} are Wigner eigentransitions, the functions on phase space corresponding to matrix transitions between oscillator states. They are well known.[16] For $r \geq s$, abusing notation,

$$f_{rs}(u) := \frac{1}{\pi}(-1)^s\sqrt{\frac{s!}{r!}}\,(2U^2)^{(r-s)/2}e^{-i(r-s)\vartheta}L_s^{r-s}(2U^2)\,e^{-U^2},$$

where $\vartheta := \arctan(P/Q)$. Then f_{sr} is the complex conjugate of f_{rs}. In (9) we proceed to sum over each subdiagonal, where $r - s = l \geq 0$:

$$\sum_{r-s=l}\sqrt{n_r n_s}f_{rs}(u_1)f_{rs}(u_2)$$

$$= \frac{n_0}{\pi^2}\,e^{-l\beta/2}(2U_1 U_2)^l e^{-il(\vartheta_1+\vartheta_2)}\,e^{-U_1^2-U_2^2}\sum_{s=0}^{\infty}\frac{s!}{(l+s)!}\,e^{-s\beta}\,L_s^l(2U_1^2)L_s^l(2U_2^2)$$

$$= \frac{1}{\pi^2}\,e^{-(U_1^2+U_2^2)/\lambda}\,e^{-il(\vartheta_1+\vartheta_2)}I_l\left(\frac{2U_1 U_2}{\sinh(\beta/2)}\right),$$

where I_l denotes the modified Bessel function, on use of another series formula:[10]

$$\sum_{n=0}^{\infty}\frac{n!}{(n+\alpha)!}L_n^{\alpha}(x)L_n^{\alpha}(y)\,t^n = \frac{(xyt)^{-\alpha/2}}{1-t}\,e^{-(x+y)t/(1-t)}\,I_\alpha\left(\frac{2\sqrt{xyt}}{1-t}\right).$$

Similarly for $r - s = -l < 0$, we get the same result replaced by its complex conjugate. Borrowing finally the generating function identity for Bessel functions,

$$I_0(z) + 2\sum_{l=1}^{\infty}I_l(z)\cos(l\theta) = e^{z\cos\theta},$$

where, by taking $\theta = \vartheta_1 + \vartheta_2 + \pi$, one obtains for the total sum:

$$\pi^{-2}e^{-[(U_1^2+U_2^2)/\lambda + 2U_1 U_2\,\text{csch}(\beta/2)\cos(\vartheta_1+\vartheta_2)]}$$

$$= \pi^{-2}e^{-\frac{1}{2}[(q_1^2+q_2^2)(\omega+\mu)+(p_1^2+p_2^2)(\omega^{-1}+\mu^{-1})]}e^{-q_1 q_2(\omega-\mu)}e^{p_1 p_2(\mu^{-1}-\omega^{-1})},$$

which in view of (4) is the correct result. Clearly the choice $\theta = \vartheta_1 + \vartheta_2 + \pi$ amounts to the *alternating sign* rule for the functional:

$$c_r = (-1)^r\sqrt{n_r}\quad\text{for}\quad r = 0, 1, 2, \ldots$$

In the end, for $P_{2\,\mathrm{SLK}}(u_1, u_2; \mathrm{spin})$ we obtain:

$$\frac{1}{2}\big(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\big)\big(\uparrow_{1'}\downarrow_{2'} - \downarrow_{1'}\uparrow_{2'}\big)\sum_{r,s=0}^{\infty}(-)^{n_r+n_s}\sqrt{n_r n_s}\,f_{rs}(u_1)f_{rs}(u_2).$$

As far as we know, this is the first time that the solution to the sign dilemma has been exhibited for any model. No big deal, a devil's advocate might say, since P_{gs} was known beforehand. But, in point of fact, the correct choice of signs may instead be chosen by optimization of the *energy functional*; so it can be found without prior knowledge of the system's ground state. Our next step is to confirm this claim.

IV. THE ENERGY FUNCTIONAL

We still work in dimension one. The energy E_{gs} of the ground state is of course $\omega/2 + \mu/2$. This contains one-body contributions $E_{1\mathrm{gs}}$ and two-body contributions $E_{2\mathrm{gs}}$. The former correspond to the kinetic and confinement energy parts. Remember first that the 1-body Hamiltonian is given by

$$h(u) = \frac{p^2}{2} + \frac{\omega^2 r^2}{2} = \sqrt{\omega\mu}\left(\frac{P^2}{2} + \frac{\omega Q^2}{2\mu}\right).$$

It is a simple exercise to obtain $E_{1\mathrm{gs}}$ by integration of expression (5) with this observable:

$$E_{1\mathrm{gs}} = \frac{\omega}{2} + \frac{\mu + \omega^2/\mu}{4}.$$

More instructive is to prove that this equals $2\sum_r n_r h_{rr}$, where h_{rr} denotes the 1-body energy associated to each natural orbital. The calculation runs as follows:

$$\begin{aligned}
2\sum_r n_r h_{rr} &= \frac{8\,\omega\mu}{(\sqrt{\omega}+\sqrt{\mu})^2}\sum_{r=0}^{\infty}\left(\frac{\sqrt{\omega}-\sqrt{\mu}}{\sqrt{\omega}+\sqrt{\mu}}\right)^{2r}\int f_{rr}(Q;P)\left(\frac{P^2}{2}+\frac{\omega Q^2}{2\mu}\right)dQ\,dP \\
&= \frac{2\,\omega\mu}{(\sqrt{\omega}+\sqrt{\mu})^2}\left(1+\frac{\omega}{\mu}\right)\sum_{r=0}^{\infty}(2r+1)\left(\frac{\sqrt{\omega}-\sqrt{\mu}}{\sqrt{\omega}+\sqrt{\mu}}\right)^{2r} \\
&= \frac{2\,\omega\mu}{(\sqrt{\omega}+\sqrt{\mu})^2}\left(1+\frac{\omega}{\mu}\right)\frac{2(\omega+\mu)(\sqrt{\omega}+\sqrt{\mu})^2}{16\omega\mu} = \frac{\omega}{2} + \frac{\mu+\omega^2/\mu}{4}.
\end{aligned}$$

We have used (8) and the identities

$$\int f_{rr}(Q;P)P^2\,dQ\,dP = \int f_{rr}(Q;P)Q^2\,dQ\,dP = r + \frac{1}{2};\qquad \sum_{r=0}^{\infty}(2r+1)x^r = \frac{1+x}{(1-x)^2}.$$

Now for the two-body contributions. The interelectronic repulsion potential in (2) is $\frac{\mu^2 - \omega^2}{4} r_{12}^2$, so these contributions are of the form $\sum_{rs} c_r c_s L_{sr}$, with the L_{sr} given by:

$$L_{sr} = \frac{\mu^2 - \omega^2}{4} \int f_{sr}(q_1; p_1) f_{sr}(q_2; p_2)(q_1 - q_2)^2 \, dq_1 \, dq_2 \, dp_1 \, dp_2$$

$$= \frac{\mu^2 - \omega^2}{4\sqrt{\omega\mu}} \int h_s(Q_1) h_r(Q_1)(Q_1 - Q_2)^2 h_s(Q_2) h_r(Q_2) \, dQ_1 \, dQ_2.$$

Here h_r are the usual harmonic oscillator eigenfunctions for unit frequency. We consider the diagonal $r = s$ first, whereby

$$L_{rr} = \frac{\mu^2 - \omega^2}{2\sqrt{\omega\mu}} \left(r + \frac{1}{2} \right); \quad \text{and thus}$$

$$\sum_r n_r L_{rr} = \frac{\mu^2 - \omega^2}{2\sqrt{\omega\mu}} \frac{4\sqrt{\omega\mu}}{(\sqrt{\omega} + \sqrt{\mu})^2} \frac{(\omega + \mu)(\sqrt{\omega} + \sqrt{\mu})^2}{16\omega\mu} = \frac{\mu^2 - \omega^2}{4\mu} \frac{\omega + \mu}{2\omega}.$$

We have used that the expected value of Q^2 for a harmonic oscillator eigenstate is $r + \frac{1}{2}$ and that the expected value of Q is zero. Notice that $\frac{\omega + \mu}{2\omega} < 1$. Therefore, to fill up the presumed energy gap $(\omega^2 - \mu^2)/4\mu$ we have to "dig deeper".

Now $\int h_s(Q) h_r(Q) \, dQ = 0$ for $s \neq r$, by orthogonality. A non-vanishing contribution of the off-diagonal part may then come (only) from the terms

$$\pm \frac{\omega^2 - \mu^2}{2\sqrt{\omega\mu}} \sqrt{n_r n_{r+1}} \left[\int h_r(Q) h_{r+1}(Q) Q \, dQ \right]^2.$$

We compute:

$$\pm \frac{\omega^2 - \mu^2}{\sqrt{\omega\mu}} \sum_{r=0}^{\infty} \sqrt{n_r n_{r+1}} \left[\int h_r(Q) h_{r+1}(Q) Q \, dQ \right]^2$$

$$= \pm \frac{\omega^2 - \mu^2}{\sqrt{\omega\mu}} \frac{4\sqrt{\omega\mu}(\sqrt{\omega} - \sqrt{\mu})}{(\sqrt{\omega} + \sqrt{\mu})^3} \sum_{r=0}^{\infty} \left(\frac{\sqrt{\omega} - \sqrt{\mu}}{\sqrt{\omega} + \sqrt{\mu}} \right)^{2r} \frac{r + 1}{2}$$

$$= \pm(\omega^2 - \mu^2) \frac{2(\sqrt{\omega} - \sqrt{\mu})}{(\sqrt{\omega} + \sqrt{\mu})^3} \frac{(\sqrt{\omega} + \sqrt{\mu})^4}{16\,\omega\mu}$$

$$= \pm \frac{\omega^2 - \mu^2}{4\mu} \frac{\omega - \mu}{2\omega}.$$

Here we employ $\sum_{r=0}^{\infty}(r + 1)x^r = (1 - x)^{-2}$. The factor $(r + 1)/2$ comes from the definition of the emission operators $a^\dagger = (Q - iP)/\sqrt{2}$ (or the absorption operators), with $a^\dagger h_r = \sqrt{r + 1}\, h_{r+1}$. There is also an overall factor of 2 coming from two subdiagonals for each r.

Obviously there are no other contributions. In order to minimize the energy we now have to choose *minus* signs whenever $s = r \pm 1$, so our contention on the alternating sign rule in

the SLK functional for the harmonium model is proved; indeed, in this section we made no use of P_{gs} whatsoever. The total energy comes out as

$$\frac{\omega}{2} + \frac{\mu + \omega^2/\mu}{4} + \frac{\mu^2 - \omega^2}{4\mu}\frac{\omega + \mu}{2\omega} - \frac{\omega^2 - \mu^2}{4\mu}\frac{\omega - \mu}{2\omega} = \frac{\omega}{2} + \frac{\mu}{2},$$

as it ought to be.

V. DISCUSSION

That's all very well, the devil's advocate now concedes. But is it not rather baroque? At the heart of density functional theory there is the proof of existence of a functional yielding the ground state energy from d_{gs}. We have managed to get it by a roundabout method equivalent to reconstructing the two-body state. Can't we just proceed directly? Yes, we can: the energy of the ground state is just (twice) the average energy of the Gibbs ensemble[19] represented by (7). To wit,

$$E_{\mathrm{gs}} = E[d_{\mathrm{gs}}] = 2\sqrt{\omega\mu}\left(\frac{1}{e^\beta - 1} + \frac{1}{2}\right) = \frac{\omega + \mu}{2}.$$

Nearly all the exchange-correlation energy functionals currently used in quantum chemistry trace their ancestry to that of Müller.[9,13–15,20] Such approximations, written in our terms, are most often of the following form:

$$\mathcal{E}_{\mathrm{xc}}[d] = -\frac{1}{2}\sum_{j,k=1}^{\infty} a(n_j, n_k)\int f_{jk}(\boldsymbol{x}_1)V\big(|\boldsymbol{r}_1 - \boldsymbol{r}_2|\big)f_{kj}(\boldsymbol{x}_2)\,d\boldsymbol{x}_1\,d\boldsymbol{x}_2,$$

with integration both on spin and orbital variables. These are all actually recipes for d_2. For the Müller functional $a(n_j, n_k) = \sqrt{n_j n_k}$. A handy list of alternatives is provided in Ref. 14. According to that reference, all of them (except for the Hartree–Fock functional) violate antisymmetry; nearly all of them violate the sum rule for d_2; as well as invariance under exchange of particles and holes for the correlation part.

It is well known that the Müller functional is overbinding. Our own rigorous proof of this fact for real two-electron atoms[21] is much more transparent than the one in Ref. 13 and shows that definite positivity of the Coulomb potential does play a decisive role, whereas the extra minus signs in Müller's functional do not. For these very reasons the Müller functional's tendency to overcorrelate needs reexamination in harmonium. Differences between Coulomb and confining potentials are of course considerable; nevertheless, detailed analytic

comparison of the proposed functionals with the exact one remains an useful exercise, throwing some light, from our viewpoint, on the elusive correlation functional. This will be done elsewhere.

Also, the remark at the beginning of this section pictures the harmonium "atom" as a system in equilibrium, with temperature depending on the strength of the interelectronic repulsion. Although matters are very different for confining potentials versus electrostatic ones, as well as for atoms with more than two electrons, it would seem to suggest that concentration on $\mathcal{E}_{\mathrm{xc}}[d]$ is a poor strategy.

The Wigner function for the Hartree–Fock state for harmonium is given by the quasiprobability

$$P_{\mathrm{HF}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) = \frac{1}{\pi^6}\, e^{-(r_1^2+r_2^2)\sqrt{(\omega^2+\mu^2)/2}}\, e^{-(p_1^2+p_2^2)/\sqrt{(\omega^2+\mu^2)/2}}$$

$$= \frac{1}{\pi^6}\, e^{-(R^2+r^2)\sqrt{(\omega^2+\mu^2)/2}} e^{-(P^2+p^2)/\sqrt{(\omega^2+\mu^2)/2}},$$

so that the expressions (6) are replaced by the rather trivial

$$A = \begin{pmatrix} \sqrt{(\omega^2+\mu^2)/2} & \\ & \sqrt{(\omega^2+\mu^2)/2} \end{pmatrix}, \quad A^{-1} = \begin{pmatrix} 1/\sqrt{(\omega^2+\mu^2)/2} & \\ & 1/\sqrt{(\omega^2+\mu^2)/2} \end{pmatrix}.$$

Coming to the correlation energy for harmonium: use of P_{HF} gives

$$\begin{aligned}
E_{\mathrm{HF}} &= \frac{1}{\pi^6} \int \left(\frac{P^2}{2} + \frac{\omega^2 R^2}{2} + \frac{p^2}{2} + \frac{\mu^2 r^2}{2} \right) \\
&\quad \times e^{-(R^2+r^2)\sqrt{(\omega^2+\mu^2)/2}} e^{-(P^2+p^2)/\sqrt{(\omega^2+\mu^2)/2}} \, d^3\boldsymbol{P}\, d^3\boldsymbol{R}\, d^3\boldsymbol{p}\, d^3\boldsymbol{r} \\
&= \frac{3\sqrt{(\omega^2+\mu^2)/2}}{4} + \frac{3\,\omega^2}{4\sqrt{(\omega^2+\mu^2)/2}} + \frac{3\sqrt{(\omega^2+\mu^2)/2}}{4} + \frac{3\mu^2}{4\sqrt{(\omega^2+\mu^2)/2}} \\
&= 3\sqrt{(\omega^2+\mu^2)/2},
\end{aligned}$$

and so the correlation energy is

$$E_c := E_0 - E_{\mathrm{HF}} = 3\left(\frac{\omega+\mu}{2} - \sqrt{\frac{\omega^2+\mu^2}{2}} \right) \sim -\frac{3\,\delta^2}{32\,\omega^3} \quad \text{as } \delta \downarrow 0.$$

March and coworkers have suggested a definition for the correlation energy density on configuration space on the basis of the Hartree–Fock wave function and the exact ground state for harmonium. However, relative momentum is as important as relative position in determining interelectronic correlation, and it seems more appealing to define a correlation

energy density on *phase space*, in the spirit of Rassolov[22] and of more recent work by Gill and coworkers.[23] We deal with this elsewhere.

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