Approximations for the interparticle interaction energy in an exactly solvable two-electron model atom

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The capability of different ansatz kernels, denoted as $K(\mathbf{r},\mathbf{r}')$, in the calculation of the electron-electron interaction energy is investigated here for an exactly solvable two-electron model atom proposed by Moshinsky. The model atom is in the spin-compensated, paramagnetic ground state. The exact expression for the interaction energy in this state, derived by the diagonal of the second-order density matrix, is used as a rigorous background for comparison. It is found that the form of $K_M(\mathbf{r},\mathbf{r}')=2\rho(\mathbf{r})\rho(\mathbf{r}')-\gamma^p(\mathbf{r},\mathbf{r}')\gamma^q(\mathbf{r}',\mathbf{r})$, expressed via the $\rho(\mathbf{r})$ density distributions and operator powers of the one-body density matrix $\gamma(\mathbf{r},\mathbf{r}')$, results in the exact value for the interparticle interaction energy of the two-electron model atom if and only if $p=q=1/2$. Approximate forms with $p=q\neq 1/2$ and with $p\neq q$ at $(p+q)=1$ give deviations from the exact expression.

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I. INTRODUCTION

In density-matrix-functional theory (DMFT), the one-electron reduced density matrix (the 1-matrix) plays the role [1] of the main variable. The external potential energy can easily be expressed in terms of the one-particle density, and going from density-functional to density-matrix-functional theory eliminates the problem of the precise determination of the kinetic energy. The electron-electron interaction energy is the *only* contribution to the total energy without a known explicit dependence on the 1-matrix. Owing to this difficulty, it has been the tendency recently [2] to use ansatz kernels $K(\mathbf{r},\mathbf{r}')$ instead of the diagonal of the second-order density matrix, i.e., to replace the so-called two-particle density $n_2(\mathbf{r},\mathbf{r}')$ by kernels constructed from the 1-matrix and its diagonal, the one-particle density.

Considering the fact that the complexity [3] of scientific progress consists of a mixture of well-designed experiments, *ab initio* microscopic calculations, and simple models, the present study is based on an exactly solvable two-electron model [4,5] introduced earlier by Moshinsky. The study is performed in a comparative manner in order to get information that would be oriented to practical applications of DMFT in other situations. Thus, we employ simple ansatz kernels to calculate approximate interparticle interaction energies of the confined two-electron system. This energy is exactly determined by the given interparticle force in coordinate space and the diagonal of the second-order density matrix of the model.

The Hamiltonian of this confined two-electron system is taken as

$$\hat{H}=-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)+\frac{1}{2}m\omega_0^2\left(\mathbf{r}_1^2+\mathbf{r}_2^2\right)+\frac{1}{2}m\Lambda\omega_0^2(\mathbf{r}_1-\mathbf{r}_2)^2, \tag{1}$$

where Λ is a convenient coupling parameter. In the noninteracting case, $\Lambda=0$. From now on we shall use Hartree atomic units, $e^2=\hbar=m=1$. The exact (ex) solution [4] for the spatial wave function of the singlet ground state of the model atom is given by

$$\psi_{\mathrm{ex}}(\mathbf{r}_1,\mathbf{r}_2)=\left(\frac{\omega_-\omega_+}{\pi^2}\right)^{D/4}e^{-\frac{1}{2}\Omega_1(r_1^2+r_2^2)}e^{\frac{1}{2}\Omega_2\mathbf{r}_1\cdot\mathbf{r}_2}, \tag{2}$$

in space dimension D. The $\Omega_1=(\omega_-+\omega_+)/2$ and $\Omega_2=(\omega_--\omega_+)$ frequencies are expressed by $\omega_+=\omega_0$ and $\omega_-=\omega_0\sqrt{1+2\Lambda}$. The ground-state energy is $E_{\mathrm{g.s.}}^{\mathrm{ex}}=(D/2)\omega_0(1+\sqrt{1+2\Lambda})$.

Section II is devoted to the theory and the obtained new results in a self-contained representation. The paper ends in Sec. III with our main conclusion.

II. THEORY AND RESULTS

We have shown [6] recently that the kernel function of the qth power of the density operator has the form

$$\gamma^q(\mathbf{r_1},\mathbf{r_2})=\left[\frac{2a-b}{\pi\lambda}\frac{(2\lambda)^{2q}}{(1+\lambda)^{2q}-(1-\lambda)^{2q}}\right]^{D/2}\times e^{-a_q(r_1^2+r_2^2)}e^{b_q\mathbf{r}_1\cdot\mathbf{r}_2}, \tag{3}$$

in terms of the informative $\lambda(\Lambda)=\sqrt{\omega_+\omega_-}/(\omega_++\omega_-)=2(1+2\Lambda)^{1/4}/(1+\sqrt{1+2\Lambda})$. Clearly, $\lambda\in[0,1]$. Here, $(2a-b)=2\omega_+\omega_-/(\omega_++\omega_-)=2\omega_0\sqrt{1+2\Lambda}/(1+\sqrt{1+2\Lambda})$. Due to the special character of the $\lambda(\Lambda)$ function, to any $-1/2<\Lambda<0$ repulsive coupling there exists a corresponding attractive one $\Lambda'>0$ for which $\lambda(\Lambda)=\lambda(\Lambda')$.

In Eq. (3), the a_q and b_q pairs are [6] determined as

$$a_q=\frac{2a+b}{4}\lambda\left[\frac{(1+\lambda)^q+(1-\lambda)^q}{(1+\lambda)^q-(1-\lambda)^q}+\frac{(1+\lambda)^q-(1-\lambda)^q}{(1+\lambda)^q+(1-\lambda)^q}\right], \tag{4}$$

$$b_q=\frac{2a+b}{2}\lambda\left[\frac{(1+\lambda)^q+(1-\lambda)^q}{(1+\lambda)^q-(1-\lambda)^q}-\frac{(1+\lambda)^q-(1-\lambda)^q}{(1+\lambda)^q+(1-\lambda)^q}\right], \tag{5}$$

where $(2a+b)=[(\omega_++\omega_-)/2]=(\omega_0/2)(1+\sqrt{1+2\Lambda})$ in terms of the physical variables. The diagonal, $\mathbf{r}_1=\mathbf{r}_2\equiv\mathbf{x}$, of the standard one-particle density matrix ($q=1$) gives the

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density distribution

$$\rho(\mathbf{x}) = \left(\frac{2a-b}{\pi}\right)^{D/2} e^{-(2a-b)x^2}. \tag{6}$$

Notice that this density distribution—similar to the exact eigenfunction, the $n_2(\mathbf{r}_1,\mathbf{r}_2) \equiv \psi^2_{\rm ex}(\mathbf{r}_1,\mathbf{r}_2)$ two-particle density [1,7], and the ground-state energy—shows a clear *difference* between the attractive ($\Lambda > 0$) and repulsive ($-0.5 < \Lambda < 0$) cases. From our previous detailed investigation [6] of different quantum entropies, we concluded that the range of $(1/2) \leqslant q < 1$ seems to be the proper one to practical applications of density matrices γ^q. The present work on interaction energies rests on this conclusion.

As we stated in the Introduction, the basic goal is to express the total energy of an interacting system in terms of one-particle density matrices. Considering the proper normalization of the inputs, this energy is described exactly by the equation

$$E^{\rm ex}_{\rm g.s.} = 2\int t(r)d\mathbf{r} + 2\frac{1}{2}\omega_0^2\int r^2\rho(r)d\mathbf{r} + \frac{1}{2}\Lambda\omega_0^2\iint(\mathbf{r}-\mathbf{r}')^2 n_2(\mathbf{r},\mathbf{r}')d\mathbf{r}\,d\mathbf{r}', \tag{7}$$

where the kinetic energy density, $t(r)$, in the first term is given [8] by the informative $t(r) = (1/2)[\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{r}'}\gamma(\mathbf{r},\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} = [|\nabla\rho|^2/(8\rho)] + b(D/2)\rho$ expression. We easily derive

$$E^{\rm ex}_{\rm g.s.}(\Lambda) = \frac{D}{4}\omega_0(1+\sqrt{1+2\Lambda}) + \frac{D}{4}\omega_0\frac{1+\sqrt{1+2\Lambda}}{\sqrt{1+2\Lambda}} + \frac{D}{2}\omega_0\frac{\Lambda}{\sqrt{1+2\Lambda}}, \tag{8}$$

in the same order of terms as in Eq. (7) for the ground-state energy [6]. This equation decomposes $E^{\rm ex}_{\rm g.s.}(\Lambda) = (D/2)\omega_0(1+\sqrt{1+2\Lambda})$, obtained from the Schrödinger Hamiltonian.

We proceed by calculating the following double integral:

$$I_{p,q}(\Lambda) \equiv \frac{1}{2}\Lambda\omega_0^2\iint(\mathbf{r}-\mathbf{r}')^2\gamma^p(\mathbf{r},\mathbf{r}')\gamma^q(\mathbf{r}',\mathbf{r})d\mathbf{r}\,d\mathbf{r}'. \tag{9}$$

Applying the convenient notations $\alpha \equiv (a_p + a_q)$ and $\eta \equiv (b_p + b_q)$, together with

$$B_\beta \equiv \left[\frac{1}{\lambda}\frac{(2\lambda)^{2\beta}}{(1+\lambda)^{2\beta}-(1-\lambda)^{2\beta}}\right]^{1/2}, \tag{10}$$

we write the result of long but straightforward integrations in Eq. (9) as

$$I_{p,q}(\Lambda) = \frac{D}{2}\Lambda\omega_0^2 B_p B_q(2a-b)\frac{4}{(2\alpha+\eta)\sqrt{4\alpha^2-\eta^2}}. \tag{11}$$

Now we introduce the obvious notation of $E^{\rm ex}_{\rm int}(\Lambda) = (D/2)\omega_0\Lambda/\sqrt{1+2\Lambda}$ for the *interparticle* interaction energy in Eq. (8) and a new [9] variable $\xi \equiv (1-\lambda)/(1+\lambda)$; $\xi \in [0,1]$. With these, we can rewrite the result in Eq. (11) into a more easily interpretable form

$$I_{p,q}(\Lambda) = \frac{1}{2}E^{\rm ex}_{\rm int}(\Lambda)\left[1+\left(\frac{1-\sqrt{\xi}}{1+\sqrt{\xi}}\right)^2\right] \times \frac{(1-\xi^p)(1-\xi^q)}{1+\xi}\frac{(1-\xi)^{p+q+1}}{(1-\xi^{p+q})^2}. \tag{12}$$

Next we evaluate the more common, density-related double integral

$$J(\Lambda) \equiv \frac{1}{2}\Lambda\omega_0^2\iint(\mathbf{r}-\mathbf{r}')^2\rho(\mathbf{r})\rho(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}', \tag{13}$$

where $\rho(\mathbf{x})$ is given by Eq. (6). After integrations, we get

$$J(\Lambda) = \frac{1}{2}E^{\rm ex}_{\rm int}(\Lambda)\left[1+\left(\frac{1-\sqrt{\xi}}{1+\sqrt{\xi}}\right)^2\right], \tag{14}$$

in terms of the notation and variable used already in Eq. (12) for $I_{p,q}(\Lambda)$. A simple inspection, based on Eqs. (12) and (14), shows that we have

$$E^{\rm ex}_{\rm int}(\Lambda) = 2J(\Lambda) - I_{p,q}(\Lambda), \tag{15}$$

for arbitrary values of the physically allowed $\Lambda \in [-0.5,\infty)$, if and only if, $p = q = 1/2$.

According to the above details, the final form for the kernel $K_M(\mathbf{r},\mathbf{r}')$ to be used in DMFT instead of the two-particle density $n_2(\mathbf{r},\mathbf{r}')$ is

$$K_M(\mathbf{r},\mathbf{r}') = 2\rho(\mathbf{r})\rho(\mathbf{r}') - \gamma^{1/2}(\mathbf{r},\mathbf{r}')\gamma^{1/2}(\mathbf{r}',\mathbf{r}). \tag{16}$$

This form, which yields the *exact* result in the investigated Moshinsky's case, was proposed earlier by Müller as an *optimal* one for a spin-compensated system [10]. Notice at this important point that the $p = q = 1/2$ prescription provides a *lower* bound in the Coulomb case to the true Schrödinger energy of confined two electrons [2]. Now, we can see that in the Moshinsky's case this bound coincides with the exact value. This is our main result.

After establishing a rigorous result, we investigate the capability of few ansatz kernels. As an illustrative comparison, we plot in Fig. 1 the function

$$F_{p,q}(\xi) \equiv \left[1+\left(\frac{1-\sqrt{\xi}}{1+\sqrt{\xi}}\right)^2\right] \times \left[1-\frac{1}{2}\frac{(1-\xi^p)(1-\xi^q)}{1+\xi}\frac{(1-\xi)^{p+q+1}}{(1-\xi^{p+q})^2}\right] \tag{17}$$

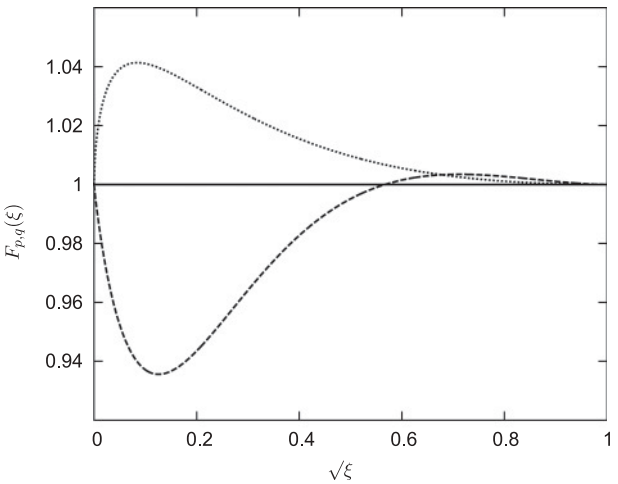

FIG. 1. The $F_{p,q}(\xi)$ function, defined by Eq. (17), as a function of $\sqrt{\xi}$ at different parametrizations. Dashed curve refers to $p = q = 0.65$; dotted curve to $p = 0.65$ and $q = 0.35$. The solid line at unity corresponds to $p = q = 1/2$, i.e., the exact representation.

for a common pair of $p = q = 0.65$ and for a different pair, i.e., $p = 0.65$ and $q = 0.35$. The former was considered [11] to be a well-designed one in a recent calculation of gaps in condensed matter, where the interparticle force is Coulombic. The latter version $(p + q = 1)$ still satisfies [2] a global integral condition for the exchange-correlation hole which is violated in the former version (symmetric: $p = q$).

There is, with $p = q = 0.65$, an interesting *oscillation* around unity. The crossing through unity appears at about $\lambda = 1/2$ in this particular case. Interestingly, one could find crossing points to any $p = q > 0$ pairs in the $0 < \xi < 1$ range, i.e., there are interparticle coupling parameters at which the so-calculated interaction energies become equal to the exact ones. The dotted curve signals that the fulfillment of an integral condition alone is not enough to obtain an exact result for the interparticle interaction energy in the $0 < \xi < 1$ range.

III. CONCLUSION

We have shown in this Brief Report that a kernel $K_M(\mathbf{r}, \mathbf{r}') = 2\rho(\mathbf{r})\rho(\mathbf{r}') - \gamma^p(\mathbf{r}, \mathbf{r}')\gamma^q(\mathbf{r}', \mathbf{r})$, expressed via the $\rho(\mathbf{r})$ density distributions and operator powers of the one-particle density matrix $\gamma(\mathbf{r}, \mathbf{r}')$, results in the exact value for the interparticle interaction energy of a two-electron model atom introduced by Moshinsky if and only if $p = q = 1/2$. Forms with $p \neq q$ at $(p + q) = 1$ and with $0.5 < p = q < 1$ give deviations from the exact expression.

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