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Explicit form of Pauli potential for direct derivation of pair density from a two-particle differential equation for the quintet state of four electrons with harmonic interparticle interactions

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Abstract   Recently, an analytic two-particle density matrix (2DM) has been derived for the quintet state of four electrons interacting via two-body harmonic forces. Here we use this 2DM to extract the exact pair density $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$. This is then employed in the known two-particle partial differential equation for the pair density amplitude to extract the Pauli potential $v_P(\mathbf{r}_1, \mathbf{r}_2)$ for this quintet state.

Keywords   Pair density · Pauli potential

1 Theory and results

A variety of uses have now been made of the Pauli potential $v_P(\mathbf{r})$ of conventional density functional theory (DFT) [1], as reviewed recently by one of us [2]. However,

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what is still lacking is the desired functional form $v_P[n]$, where the ground-state density $n(\mathbf{r})$ is, of course, the main tool of DFT.

More recently, some interest has been focussed on the pair density functional description [3,4]. There, a generalized Pauli potential has been defined in order to write a two-particle differential equation for the pair density amplitude, say $\chi(\mathbf{r}_1, \mathbf{r}_2)$, in an N-electron problem [3,5].

But progress on the form of $v_P(\mathbf{r}_1, \mathbf{r}_2)$ to enable the direct derivation of $\chi(\mathbf{r}_1, \mathbf{r}_2)$ from such a two-particle differential equation has proved to be slow. Therefore, in this note, we shall utilize the work of Akbari et al. [6], in which a model analytical two-particle density matrix (2DM) $\Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2')$ was presented for four electrons in the quintet state interacting via two-body harmonic forces. The diagonal element of this Γ is, of course, the desired pair density $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ which has a simple, translationally invariant form $\Gamma(r_{12})$, r_{12} being the distance $|\mathbf{r}_1 - \mathbf{r}_2|$, which is a product of r_{12}^2 and a Gaussian factor having also the argument proportional to r_{12}^2.

Below, using this exactly known model form, we shall extract the form of the Pauli potential, namely $v_P(\mathbf{r}_1, \mathbf{r}_2)$, from the above form of $\Gamma(r_{12})$ using the two-particle differential equation given by Nagy and Amovilli [3]. This takes the explicit form, in atomic units ($\hbar = 1$, $m = 1$), for the four-particle model under discussion:

$$\left\{ -\frac{1}{2}\left[\nabla_1^2 + \nabla_2^2 \right] + \frac{3}{2}\kappa r_{12}^2 + v_P(\mathbf{r}_1, \mathbf{r}_2) \right\} \chi(\mathbf{r}_1, \mathbf{r}_2) = \mu \, \chi(\mathbf{r}_1, \mathbf{r}_2). \qquad (1)$$

We remind that in this equation the external potential has been set to zero by taking the limit of the external harmonic force constant k_{ext} to 0^+.

This is the point at which we must be quite explicit about the way the pair density $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ to be utilized below is derived. The origin is an admittedly somewhat simplistic model due to Bruch [7]. This author considers four electrons moving under the influence of a central pairwise interaction $v(r_{ij})$ given by

$$v(r_{ij}) = \frac{1}{2}\kappa r_{ij}^2. \qquad (2)$$

In the following discussion of the Pauli potential $v_P(\mathbf{r}_1, \mathbf{r}_2)$, we shall restrict ourselves to the quintet state, $S = 2$, for which the exact wave function $\Psi^{(2S+1)} = \Psi^{(5)}$ is known from the work of Bruch [7]. The form of $\Psi^{(5)}$ is then given in this reference as the product of a spatial wave function quoted below, and a spin function. We shall work below with the reduced spatial density matrices Γ_n of Löwdin [8], to be derived from the Bruch spatial wave function $\Psi^{(5)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$ having the explicit, unnormalized form

$$\Psi^{(5)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \mathbf{u} \cdot (\mathbf{v} \times \mathbf{w}) \exp Q. \qquad (3)$$

Bruch gives the RHS of Eq. (3) quite explicitly by defining $\mathbf{u}$ to Q in the following fashion [7]:

$$\mathbf{u} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) - \frac{1}{2}(\mathbf{r}_3 + \mathbf{r}_4), \qquad (4)$$

$$\mathbf{v} = \mathbf{r}_1 - \mathbf{r}_2, \quad \mathbf{w} = \mathbf{r}_3 - \mathbf{r}_4, \tag{5}$$

and

$$Q = -\frac{\sqrt{\kappa}}{4} \left(2u^2 + v^2 + w^2 \right). \tag{6}$$

Following, for instance, Dawson and March [9], one can reduce the Scrödinger equation satisfied by (3) into an equation relating the reduced density matrices $\Gamma^{(3)}$, $\Gamma^{(2)}$ and $\Gamma^{(1)}$. In this way, Akbari et al. [6] integrated $\Gamma^{(3)}$ to obtain the exact correlated $\Gamma^{(2)}$ as

$$\Gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \propto \left\{ \left(1 - \frac{\sqrt{\kappa}}{4} |\mathbf{R} - \mathbf{R}'|^2 \right) \mathbf{r} \cdot \mathbf{r}' + (\mathbf{R} \cdot \mathbf{r})(\mathbf{R} \cdot \mathbf{r}') + (\mathbf{R}' \cdot \mathbf{r}')(\mathbf{R}' \cdot \mathbf{r}) \right.$$

$$\left. -(\mathbf{R}' \cdot \mathbf{r})(\mathbf{R} \cdot \mathbf{r}') - (\mathbf{R} \cdot \mathbf{r})(\mathbf{R}' \cdot \mathbf{r}') \right\} \exp \left[-\frac{\sqrt{\kappa}}{4} \left(|\mathbf{R} - \mathbf{R}'|^2 + r^2 + r'^2 \right) \right]. \tag{7}$$

Here $\mathbf{r}$ and $\mathbf{R}$ are defined by

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \quad \mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \tag{8}$$

the primed quantities $\mathbf{r}'$ and $\mathbf{R}'$ being defined in a parallel manner from $\mathbf{r}'_1$ and $\mathbf{r}'_2$.

Returning at this point to the pair density Γ in Eq. (1), we have the definition

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \Gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \tag{9}$$

and hence it follows almost immediately from Eqs. (7) and (9) that the pair density is given by

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) \propto |\mathbf{r}_1 - \mathbf{r}_2|^2 \exp \left(-\frac{\sqrt{\kappa}}{2} |\mathbf{r}_1 - \mathbf{r}_2|^2 \right). \tag{10}$$

With the above background, it remains to extract the Pauli potential $v_P(\mathbf{r}_1, \mathbf{r}_2)$ from Eqs. (1), (3) and (10) for the above quintet state of the Bruch model [7]. In terms of variables defined in Eq. (8), by writing

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \Gamma^{1/2}(r) \, e^{i\mathbf{P} \cdot \mathbf{R}}, \tag{11}$$

which gives back Γ as $\chi^* \chi$ and is perfectly consistent with our translationally invariant model example, we are then led, almost immediately to the equation defining $v_P(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\left[-\nabla^2 + \frac{3}{2}\kappa r^2 + v_P \right] \Gamma^{1/2}(r) = \mu \, \Gamma^{1/2}(r). \tag{12}$$

Fig. 1 Plot of the Pauli
potential derived from the pair
density of the quintet state of
four electrons interacting via
harmonic potential energy
$(1/2)\kappa r^2$ against interparticle
separation r. *Curves A, B* and *C*
refer, respectively, to the cases
with $\kappa = 0.5, 1$ and 2 a.u.
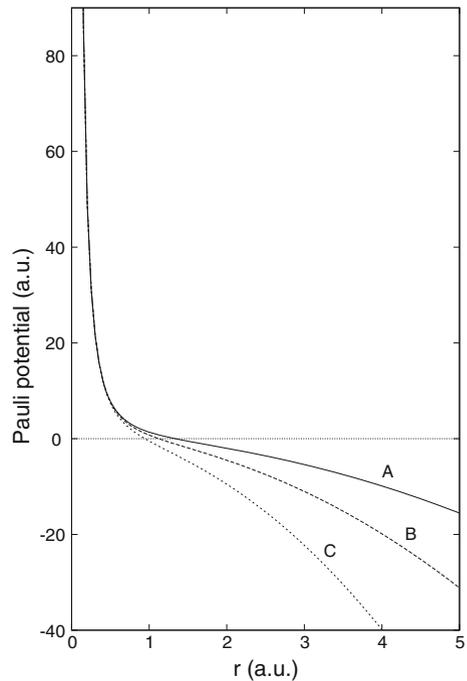
Thanks to the particular form of the solution $\Gamma^{1/2}(r)$, it is a straightforward matter to
perform the Laplacian differentiation on the LHS of the Eq. (12) and thereby, after
some manipulation (see, for example, Makarewicz [10]), to extract the desired analytic
form of the Pauli potential as

$$v_P(r) = \frac{2}{r^2} - \frac{5}{4}\kappa r^2. \tag{13}$$

Moreover, μ in Eq. (1) turns out to be $(5/2)\kappa^{1/2}$. By way of example, we show in
Fig. 1 the plot of $v_P(r)$ against r for three cases corresponding to $\kappa = 0.5, 1$ and 2
atomic units.

In summary, we have used the Bruch model [7] with spatial wave function $\Psi^{(5)}$
quoted in Eq. (3) above, together with the Nagy and Amovilli [3] form of $v_P(r_{12})$,
to extract this Pauli potential in the exact analytical form (13). This, to our present
knowledge, is the first time $v_P(r_{12})$ has been calculated exactly as a simple route to the
generation of the pair density. Of course, to complete the Nagy and Amovilli theory
of the pair density amplitude χ, we would eventually need $v_P[\Gamma](\mathbf{r}_1, \mathbf{r}_2)$ rather than
$v_P(r_{12})$ calculated above for the Bruch model. In this particular case some progress in
this direction through Eqs. (10) and (13) is, in principle, achievable but with no claim
that the resulting $v_P[\Gamma](\mathbf{r}_1, \mathbf{r}_2)$ is the desired "universal functional".

References

1. R.G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989)
2. N.H. March, J. Mol. Struct. (THEOCHEM) **943**, 77 (2010)
3. Á. Nagy, C. Amovilli, J. Chem. Phys. **121**, 6640 (2004)
4. Á. Nagy, C. Amovilli, J. Chem. Phys. **128**, 114115 (2008)
5. C. Amovilli, Á. Nagy, J. Chem. Phys. **129**, 204108 (2008)
6. A. Akbari, C. Amovilli, N.H. March, A. Rubio, Chem. Phys. Lett. **536**, 162 (2012)
7. L.W. Bruch, J. Chem. Phys. **72**, 5511 (1980)
8. P.O. Löwdin, Phys. Rev. **97**, 1474 (1955)
9. K.A. Dawson, N.H. March, J. Chem. Phys. **81**, 5850 (1984)
10. J. Makarewicz, Am. J. Phys. **54**, 178 (1986)