PHYSICAL REVIEW A **103**, 052221 (2021)

Pauli exclusion operator: An example of Hooke's atom

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(Received 22 January 2021; accepted 3 May 2021; published 28 May 2021)

The Pauli exclusion operator (PEO), which ensures proper symmetry of the eigenstates of multi-electron systems with respect to the exchange of each pair of electrons, is introduced. Once PEO is added to the Hamiltonian, no additional constraints on the multi-electron wave function due to the Pauli exclusion principle are needed. For two-electron states in two dimensions (2D) the PEO can be expressed in a closed form in terms of momentum operators, while in the position representation PEO is a nonlocal operator. Generalizations of PEO for multi-electron systems are introduced. Several approximations to PEO are discussed. Examples of analytical and numerical calculations of PEO are given for the isotropic and anisotropic Hooke's atom in 2D. The application of approximate and kernel forms of PEO for calculations of energies and states in a 2D Hooke's atom are analyzed. The relation of PEO to standard variational calculations with the use of Slater determinant is discussed.

DOI: 10.1103/PhysRevA.103.052221

I. INTRODUCTION

Two-electron systems, e.g., the He atom, were analyzed from the early years of quantum mechanics [1–3]. Since the exact solutions of such situation are not known, the energies of low states and the corresponding wave functions using the variational method are usually calculated. To be consistent with the Pauli exclusion principle [4,5] first the spin state of the electron pair is selected, which is either a singlet or a triplet, and then the trial functions of two electrons to be either symmetric or antisymmetric with respect to exchange of the two particles is assumed. This approach was successfully applied to the ground energy of the He atom as well as to its excited states [6,7].

The Pauli exclusion principle can be introduced to the variational calculations by choosing the trial function of the required symmetry with respect to the exchange of electrons. This approach may not be used in a numerical integration of the Schrödinger equation of the two-electron systems since this equation does not include terms which can be related to the Pauli exclusion principle. Then, if this equation is integrated for two electrons or for two nonfermions having the same charges and masses as the electrons, then in both cases the same energies and states are obtained.

However, for the two-electron case some calculated states do not fulfill the Pauli exclusion principle and such states have to be eliminated as nonphysical ones. As an example, wave functions symmetric with respect to the exchange of electrons are allowed for the singlet, but have to be eliminated for the triplet.

It can then be stated that, beyond the external potential and the Coulomb repulsion, there exists an additional spin-dependent field acting on both electrons which eliminates some states from the spectrum of the Hamiltonian $\hat{H}$. The presence of this field can be included in the model by introducing a spin-dependent operator $\hat{P}$ responsible for the existence of the Pauli exclusion principle. The final effect of the operators $\hat{H}$ and $\hat{P}$ acting on the eigenstate $|\Psi(1,2)\rangle$ of $\hat{H}$ is that the states of the proper electron exchange symmetry are not altered, but those of the improper symmetry vanish. Then, by numerically solving the Schrödinger equation with the operator $(\hat{H}-\hat{P})$ instead of $\hat{H}$

$$(\hat{H}-\hat{P})|\Psi(1,2)\rangle = E|\Psi(1,2)\rangle, \tag{1}$$

the states fulfilling the Pauli exclusion principle are automatically obtained and no additional constraints on the multi-electron wave function due to the Pauli exclusion principle are needed. The main purpose of this work is to analyze the operator $\hat{P}$ [further called the Pauli exclusion operator (PEO)], in several two-electron systems. We show that in these cases it is possible to obtain PEO in a closed form. We also discuss the generalization of PEO for the multi-electron case and propose several approximations of this operator. Note that PEO exists in the literature in a different meaning and it was used to calculate nuclear matter [8–10], see the discussion in Sec. V.

It is impossible to obtain PEO for the He atom for two reasons. First, the Schrodinger equation for He atom does not separate into a sum of two one-electron equations, so the eigenequation in the six-dimensional space has to be solved numerically. Second, in the presence of the attractive Coulomb potential of the He nucleus there exist both localized and delocalized electron states, and it is difficult to be treat the delocalized states numerically.

There exists a model in which the above problems can be avoided. This system, called the Hooke's atom, consists of two electrons in the field of an N-dimensional harmonic oscillator [11–15]. In this model the Schrödinger equation separates into two equations of the center-of-mass and relative

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motion of electrons. For potentials with a radial symmetry, two one-dimensional equations, which are much easier to solve numerically, are obtained. For a sufficiently strong harmonic potential, the spectrum of the Hooke's atom consists of the localized states alone. For these reasons we analyze here the PEO in the Hooke's atom model and then generalize the obtained results for the multi-electron case.

The work is organized as follows. In Sec. II we introduce the Pauli exclusion operator for two-dimensional (2D) two-electron systems. In Sec. III we generalize the PEO for multi-electron systems and propose several approximations of the PEO. In Sec. IV we show examples of the PEO in two 2D Hooke's atoms and calculate them analytically and numerically. In the same section we show examples of approximate formulas for PEO. In Sec. V we discuss the obtained results, while in the Appendixes we describe a numerical method of obtaining low- and high-energy states of the Hooke's atom and provide auxiliary formulas. The work is concluded by a summary in Sec. VI.

II. TWO-ELECTRON SYSTEMS

In the atomic units the Hamiltonian of two interacting electrons in the presence of an external potential $U(\boldsymbol{r})$ reads

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + U(\boldsymbol{r}_1) + U(\boldsymbol{r}_2). \tag{2}$$

We consider a 2D case. The description given in Eq. (2) is not complete because the solutions have to be limited to those fulfilling the Pauli exclusion principle. The two-electron wave function $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ being the eigenstate of $\hat{H}$ should be either symmetric (for the singlet state) or antisymmetric (for triplet states) with respect to the exchange $\boldsymbol{r}_1 \Leftrightarrow \boldsymbol{r}_2$. We introduce the center-of-mass $\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$ and the relative motion $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$. In the new coordinates the exchange of electrons does not affect $\boldsymbol{R}$ but changes the sign of $\boldsymbol{r}$, i.e., $\boldsymbol{r} \to -\boldsymbol{r}$. Then there is

$$\Psi(\boldsymbol{R}, -\boldsymbol{r}) = \begin{cases} \Psi(\boldsymbol{R}, \boldsymbol{r}) & \text{for singlet,} \\ -\Psi(\boldsymbol{R}, \boldsymbol{r}) & \text{for triplets.} \end{cases} \tag{3}$$

In the circular coordinates $\boldsymbol{r} = (r, \phi)$ the change $\boldsymbol{r} \to -\boldsymbol{r}$ corresponds to the transformation $(r, \phi) \to (r, \phi + \pi)$. We introduce symmetric (even in $\boldsymbol{r}$) and antisymmetric (odd in $\boldsymbol{r}$) parts of $\Psi(\boldsymbol{R}, r, \phi)$

$$\Psi(\boldsymbol{R}, r, \phi)^e = \tfrac{1}{2}[\Psi(\boldsymbol{R}, r, \phi) + \Psi(\boldsymbol{R}, r, \phi + \pi)], \tag{4}$$

$$\Psi(\boldsymbol{R}, r, \phi)^o = \tfrac{1}{2}[\Psi(\boldsymbol{R}, r, \phi) - \Psi(\boldsymbol{R}, r, \phi + \pi)]. \tag{5}$$

Because of the existence of the Pauli exclusion principle two separate eigenproblems for $\Psi(\boldsymbol{R}, r, \phi)^\eta$ (with $\eta \in \{e, o\}$) are obtained

$$\hat{H}\Psi(\boldsymbol{R}, r, \phi)^\eta = E^\eta \Psi(\boldsymbol{R}, r, \phi)^\eta, \tag{6}$$

instead of the single problem for $\Psi(\boldsymbol{R}, r, \phi)$. We can introduce the spin-dependent operator $\hat{P}$, which we call the Pauli exclusion operator (PEO), which, for a given combination of electron spins, removes the even or odd states from the spectrum of $\hat{H}$. We define $\hat{P}$ as [see Eq. (6)]

$$(\hat{H} - \hat{P})\Psi(\boldsymbol{R}, r, \phi) = \hat{H}\Psi(\boldsymbol{R}, r, \phi)^e, \tag{7}$$

for a symmetric function of spins $\hat{s}_1, \hat{s}_2$, and

$$(\hat{H} - \hat{P})\Psi(\boldsymbol{R}, r, \phi) = \hat{H}\Psi(\boldsymbol{R}, r, \phi)^o, \tag{8}$$

for the antisymmetric function of $\hat{s}_1, \hat{s}_2$. In Eqs. (7) and (8) the operator $(\hat{H} - \hat{P})$ acts on $\Psi(\boldsymbol{R}, r, \phi)$, while the operator $\hat{H}$ in Eq. (6) acts on $\Psi(\boldsymbol{R}, r, \phi)^\eta$. In their spectrums the operators $\hat{P}$ and $(\hat{H} - \hat{P})$ contain states having opposite symmetry with respect to a change $\boldsymbol{r} \to -\boldsymbol{r}$, and the sets of states belonging to both operators are disjointed. A closed form of $\hat{P}$ for multi-electron systems is unknown, but for two-electron Hamiltonians in 2D we can express $\hat{P}$ in terms of differential operators and as a nonlocal operator in the position representation.

To find the spectrum of $\hat{P}$ we introduce two auxiliary operators $\hat{P}^e$ and $\hat{P}^o$. Let $\hat{P}^e$ equal $\hat{P}$ in Eq. (7) and $\hat{P}^o$ in Eq. (8). Let $|\mathrm{n}\rangle$ and E_n be the states and energies of $\hat{H}$, respectively. Here n denotes all quantum numbers describing localized and delocalized states of $\hat{H}$. Then $\hat{H} = \sum_\mathrm{n} E_\mathrm{n}|\mathrm{n}\rangle\langle\mathrm{n}|$, and

$$\hat{P}^e = \sum_{\text{even states}} E_\mathrm{n}|\mathrm{n}\rangle\langle\mathrm{n}|, \tag{9}$$

$$\hat{P}^o = \sum_{\text{odd states}} E_\mathrm{n}|\mathrm{n}\rangle\langle\mathrm{n}|, \tag{10}$$

where "even" and "odd" states mean that in the summations we restrict ourselves to states being even or odd functions of $\boldsymbol{r}$, respectively. The above form of operators $\hat{P}^e$ and $\hat{P}^o$ is useful if all the energies and states of $\hat{H}$ are known. Examples of such calculations are presented in the next section. The operators $\hat{P}^e$ and $\hat{P}^o$ are on the same order as $\hat{H}$ and they may not be treated as perturbations to $\hat{H}$. Operator $\hat{P}$ depends on the Hamiltonian of the system.

On the left sides of Eqs. (7) and (8) there is the function $\Psi(\boldsymbol{R}, r, \phi)$ while on the right sides there are functions $\Psi(\boldsymbol{R}, r, \phi)^e$ or $\Psi(\boldsymbol{R}, r, \phi)^o$. To find a more symmetric form of these equations let us insert $\hat{P}^e$ in Eq. (9) into Eq. (7). Then we have

$$\begin{aligned}(\hat{H} - \hat{P}^e)|\Psi\rangle &= \sum_\mathrm{n} E_\mathrm{n}|\mathrm{n}\rangle\langle\mathrm{n}|\Psi\rangle - \sum_{\text{even states}} E_\mathrm{n}|\mathrm{n}\rangle\langle\mathrm{n}|\Psi\rangle \\ &= \sum_{\text{odd states}} E_\mathrm{n}|\mathrm{n}\rangle\langle\mathrm{n}|\Psi\rangle.\end{aligned} \tag{11}$$

If $|\Phi\rangle$ is an eigenstate of $\hat{H}$ with energy E then we obtain from Eq. (11)

$$(\hat{H} - \hat{P}^e)\Psi(\boldsymbol{R}, r, \phi) = \begin{Bmatrix} E \\ 0 \end{Bmatrix}\Psi(\boldsymbol{R}, r, \phi), \quad \begin{Bmatrix} \Psi = \Psi^o \\ \Psi \neq \Psi^o \end{Bmatrix}. \tag{12}$$

As seen from Eq. (12), the even parts of $\Psi(\boldsymbol{R}, r, \phi)$ are annihilated by the $(\hat{H} - \hat{P}^e)$ operator, while the odd parts of $\Psi(\boldsymbol{R}, r, \phi)$ satisfy the Schrödinger-like equation. For $\hat{P}^o$ we find

$$(\hat{H} - \hat{P}^o)\Psi(\boldsymbol{R}, r, \phi) = \begin{Bmatrix} E \\ 0 \end{Bmatrix}\Psi(\boldsymbol{R}, r, \phi), \quad \begin{Bmatrix} \Psi = \Psi^e \\ \Psi \neq \Psi^e \end{Bmatrix}. \tag{13}$$

Equations (12) and (13) can be treated as alternative definitions of the $\hat{P}^e$ and $\hat{P}^o$ operators.

Consider the functions Ψ, Ψ^o, and Ψ^e in Eqs. (4) and (5). Let $\hat{T}_{\boldsymbol{a}}$ be the translation operator $\hat{T}_{\boldsymbol{a}} w(\boldsymbol{r}) = w(\boldsymbol{r} + \boldsymbol{a})$. Then we have [16]

$$\hat{T}_{\boldsymbol{a}} = \exp(-i\boldsymbol{a}\hat{\boldsymbol{p}}/\hbar), \tag{14}$$

where $\hat{\boldsymbol{p}} = (\hbar/i)\hat{\nabla}_{\boldsymbol{r}}$ is the canonical momentum. Applying the above definition to the ϕ coordinate in $\Psi(\boldsymbol{R}, r, \phi)$ we obtain from Eqs. (4), (5), and (14)

$$\Psi(\boldsymbol{R}, r, \phi)^e = \tfrac{1}{2}(\hat{I} + e^{-i\pi r\hat{p}_\phi/\hbar})\Psi(\boldsymbol{R}, r, \phi), \tag{15}$$

$$\Psi(\boldsymbol{R}, r, \phi)^o = \tfrac{1}{2}(\hat{I} - e^{-i\pi r\hat{p}_\phi/\hbar})\Psi(\boldsymbol{R}, r, \phi), \tag{16}$$

where $\hat{p}_\phi = (\hbar/ir)(\partial/\partial\phi)$ is the angular component of the momentum and $\hat{I}$ is the unity operator. We introduce two auxiliary operators

$$\hat{A}^e = \tfrac{1}{2}(\hat{I} + e^{-i\pi r\hat{p}_\phi/\hbar}), \tag{17}$$

$$\hat{A}^o = \tfrac{1}{2}(\hat{I} - e^{-i\pi r\hat{p}_\phi/\hbar}). \tag{18}$$

Then we have from Eqs. (7), (8), and (15) to (18)

$$(\hat{H} - \hat{P}^e)\Psi(\boldsymbol{R}, r, \phi) = \hat{H}[\hat{A}^o\Psi(\boldsymbol{R}, r, \phi)], \tag{19}$$

$$(\hat{H} - \hat{P}^o)\Psi(\boldsymbol{R}, r, \phi) = \hat{H}[\hat{A}^e\Psi(\boldsymbol{R}, r, \phi)]. \tag{20}$$

The meaning of Eq. (19) is that the operator $(\hat{H} - \hat{P}^e)$, which has only odd states, acting on a general function $\Psi(\boldsymbol{R}, r, \phi)$ gives the same result as the Hamiltonian $\hat{H}$ acting on $\hat{A}^o\Psi(\boldsymbol{R}, r, \phi)$, which is an odd part of $\Psi(\boldsymbol{R}, r, \phi)$. Solving Eqs. (19) and (20) for $\hat{P}^e$ and $\hat{P}^o$ we find

$$\hat{P}^e = \tfrac{1}{2}\hat{H}(\hat{I} + e^{-i\pi r\hat{p}_\phi/\hbar}), \tag{21}$$

$$\hat{P}^o = \tfrac{1}{2}\hat{H}(\hat{I} - e^{-i\pi r\hat{p}_\phi/\hbar}). \tag{22}$$

Introducing the total spin $\hat{S} = \hat{s}_1 + \hat{s}_2$ we obtain

$$\hat{P} = \tfrac{1}{2}\hat{H}\big(\hat{I} + (-1)^{2\hat{S}_z}e^{-i\pi r\hat{p}_\phi/\hbar}\big). \tag{23}$$

Operators $\hat{P}^e$, $\hat{P}^o$, and $\hat{P}$ defined in Eqs. (21) to (23) act on the function $\Psi(\boldsymbol{R}, r, \phi)$. The representation of $\hat{P}$, as given in Eqs. (21) to (23), exists only in 2D, see the discussion in Sec. V. Inserting $\hat{P}$ from Eq. (23) into Eqs. (7) and (8) the Schrödinger equation for $\Psi(\boldsymbol{R}, r, \phi)^\eta$ is not obtained, but the differential equations of higher order in $\hat{p}_\phi$ are since

$$e^{-i\pi r\hat{p}_\phi/\hbar} = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{-i\pi r\hat{p}_\phi}{\hbar}\right)^n. \tag{24}$$

The presence of $\hat{p}_\phi$ in the exponents in Eqs. (21) to (23) causes a nonlocality of $\hat{P}$ in the position representation. Using the notation $|\boldsymbol{Q}\rangle = |\boldsymbol{R}, \boldsymbol{r}\rangle$ and $d\boldsymbol{Q} = d^2\boldsymbol{R}d^2\boldsymbol{r}$ the matrix element of $\hat{P}^e$ in Eq. (21) between two $|\boldsymbol{Q}\rangle$ states is

$$\langle\boldsymbol{Q}|\hat{P}^e|\boldsymbol{Q}'\rangle = \int d\boldsymbol{Q}''\langle\boldsymbol{Q}|\hat{H}|\boldsymbol{Q}''\rangle\langle\boldsymbol{Q}''|\frac{1}{2}(\hat{I} + e^{-i\pi r\hat{p}_\phi/\hbar})|\boldsymbol{Q}'\rangle, \tag{25}$$

and similarly for $\hat{P}^o$. In the position representation $\hat{H}$ in Eq. (2) is a local operator, so that $\langle\boldsymbol{Q}|\hat{H}|\boldsymbol{Q}''\rangle = \hat{H}_{\boldsymbol{QQ}}\delta(\boldsymbol{Q} - \boldsymbol{Q}'')$. The translation $e^{-i\pi r\hat{p}_\phi/\hbar}$ in Eq. (21) has nonzero elements between states $|\boldsymbol{R}, r, \phi\rangle$ and $|\boldsymbol{R}, r, \phi + \pi\rangle$, (for $0 \leqslant \phi < 2\pi$), i.e., between states $|\boldsymbol{R}, \boldsymbol{r}\rangle$ and $|\boldsymbol{R}, -\boldsymbol{r}\rangle$. This gives

$$\langle\boldsymbol{Q}|\hat{P}^e|\boldsymbol{Q}'\rangle = \tfrac{1}{2}\hat{H}_{\boldsymbol{QQ}}\delta(\boldsymbol{R} - \boldsymbol{R}')[\delta(\boldsymbol{r} - \boldsymbol{r}') + \delta(\boldsymbol{r} + \boldsymbol{r}')], \tag{26}$$

$$\langle\boldsymbol{Q}|\hat{P}^o|\boldsymbol{Q}'\rangle = \tfrac{1}{2}\hat{H}_{\boldsymbol{QQ}}\delta(\boldsymbol{R} - \boldsymbol{R}')[\delta(\boldsymbol{r} - \boldsymbol{r}') - \delta(\boldsymbol{r} + \boldsymbol{r}')]. \tag{27}$$

From the above equations we have, see Eq. (23),

$$\begin{aligned}\langle\boldsymbol{R}, \boldsymbol{r}|\hat{P}|\boldsymbol{R}', \boldsymbol{r}'\rangle = {}& \tfrac{1}{2}\langle\boldsymbol{R}, \boldsymbol{r}|\hat{H}|\boldsymbol{R}', \boldsymbol{r}'\rangle\,\delta(\boldsymbol{R} - \boldsymbol{R}')\\ &\times[\delta(\boldsymbol{r} - \boldsymbol{r}') + (-1)^{2\hat{S}_z}\delta(\boldsymbol{r} + \boldsymbol{r}')].\end{aligned} \tag{28}$$

In the position representation a nonlocal equation for the energy levels and wave functions is obtained

$$\hat{H}\Psi(\boldsymbol{Q}) - \int d^2\boldsymbol{Q}'\langle\boldsymbol{Q}|\hat{P}|\boldsymbol{Q}'\rangle\Psi(\boldsymbol{Q}') = \begin{Bmatrix}E\\0\end{Bmatrix}\Psi(\boldsymbol{Q}), \tag{29}$$

which resembles the Yamaguchi equation [17]. The second term in Eq. (29) describes a correction to the two-particle Hamiltonian $\hat{H}$ due to presence of the Pauli exclusion principle. Equations (28) and (29) completely describe the system because they contain *all* the information necessary to solve the two-electron problem including the limitations resulting from the Pauli exclusion principle. Once $\hat{P}$ is added to the Hamiltonian, no additional conditions on multi-electron wave function are needed.

Equations (26) to (28) suggest that in the position representation in one (1D) and three dimensions (3D) the PEO for two-electron systems have similar forms. The examples in Sec. IV confirm this observation.

III. MULTI-ELECTRON SYSTEMS

In this section we generalize the PEO for systems having more electrons. The results are more formal and abstract than those obtained for two-electron systems. Below we provide a definition of PEO for an arbitrary multi-electron Hamiltonian, but the remaining definition will relate to three-electron systems.

A. General results

Let $\hat{\Pi}_{ij}$ be the operator exchanging positions of two particles

$$\hat{\Pi}_{ij}|\boldsymbol{r}_i\boldsymbol{r}_j\rangle = |\boldsymbol{r}_j\boldsymbol{r}_i\rangle. \tag{30}$$

This operator can be expressed as an infinite series of position and momentum operators. In 1D there is [18]

$$\hat{\Pi}_{ij} = \sum_{n=0}^{\infty}\left(\frac{1}{n!}\right)\left(\frac{i}{\hbar}\right)^n(\Delta\hat{p}_x)^n(\Delta\hat{r}_x)^n, \tag{31}$$

where $\Delta\hat{r}_x = \hat{r}_{jx} - \hat{r}_{ix}$ and $\Delta\hat{p}_x = \hat{p}_{jx} - \hat{p}_{ix}$. The series for $\hat{\Pi}_{ij}$ in 2D and 3D are given in Appendix A.

Let $|\sigma_i\sigma_j\rangle$ be a state of two electron spins. The operator Σ_{ij} exchanging the spins is, see Appendix A,

$$\hat{\Sigma}_{ij} = \tfrac{1}{2} + 2(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j). \tag{32}$$

Then the operator exchanging two electrons is

$$\hat{\chi}_{ij} = \hat{\Pi}_{ij}\hat{\Sigma}_{ij}. \tag{33}$$

Let $|\mathrm{n}\rangle$ be a state vector of $k \geqslant 2$ electrons

$$\begin{aligned}\langle\boldsymbol{r}_1\sigma_1, \ldots, \boldsymbol{r}_k\sigma_k|\mathrm{n}\rangle &= \Psi(\boldsymbol{r}_1\sigma_1, \ldots, \boldsymbol{r}_k\sigma_k)\\ &= \Psi(1, \ldots, k).\end{aligned} \tag{34}$$

Then we define PEO as

$$(\hat{H}-\hat{\mathcal{P}})\Psi(1,\dots,k)=\hat{H}\left(\prod_{i=1,j>i}^{k}\hat{\chi}_{ij}\Psi(1,\dots,k)\right). \tag{35}$$

The physical meaning of $\hat{\mathcal{P}}$ is that the operator $(\hat{H}-\hat{\mathcal{P}})$ acting on unrestricted function $\Psi(1,\dots,k)$ gives the same result as the Hamiltonian $\hat{H}$ acting on a function that is antisymmetric with respect to the exchange of all pairs of electrons. Note that $\hat{\mathcal{P}}$ in Eq. (35) is defined in a different way than $\hat{P}^e$ and $\hat{P}^o$ in Eqs. (7) and (8), see the discussion in Sec. V. By solving Eq. (35) we obtain

$$\hat{\mathcal{P}}\Psi(1,\dots,k)=\left[\hat{H}\left(\hat{I}-\prod_{i=1,j>i}^{k}\hat{\chi}_{ij}\right)\right]\Psi(1,\dots,k). \tag{36}$$

Equation (36) generalizes Eqs. (19) and (20) for the multi-electron case. Let $\{|\mathrm{n}\rangle\}$ and $\{E_\mathrm{n}\}$ be the complete sets of states and energies of multi-electron Hamiltonian $\hat{H}$, respectively. Let $\{|\mathrm{n}^a\rangle\}$ be a subset of $\{|\mathrm{n}\rangle\}$ including states antisymmetric with respect to the exchange of all pairs of electrons $(\boldsymbol{r}_i\sigma_i)\Leftrightarrow(\boldsymbol{r}_j\sigma_j)$ for $1\leqslant i,j\leqslant k$. Then the PEO is

$$\hat{\mathcal{P}}=\sum_\mathrm{n}E_\mathrm{n}(|\mathrm{n}\rangle\langle\mathrm{n}|-|\mathrm{n}^a\rangle\langle\mathrm{n}^a|)=\sum_{\mathrm{n}\notin\{\mathrm{n}^a\}}E_\mathrm{n}|\mathrm{n}\rangle\langle\mathrm{n}|. \tag{37}$$

As seen from Eq. (37), the spectral resolution of PEO includes all states of $\hat{H}$ except those that are antisymmetric with respect to the exchange of all pairs of electrons. Equation (37) generalizes Eqs. (9) and (10) for multi-electron systems. To find the analog of Eqs. (12) and (13) we insert Eqs. (34) and (37) into Eq. (35) and obtain

$$(\hat{H}-\hat{\mathcal{P}})|\mathrm{n}\rangle=\begin{bmatrix}E_\mathrm{n}\\0\end{bmatrix}|\mathrm{n}\rangle, \tag{38}$$

where the upper identity holds for $|\mathrm{n}\rangle\in\{|\mathrm{n}^a\rangle\}$ and the lower one for $|\mathrm{n}\rangle\notin\{|\mathrm{n}^a\rangle\}$. As follows from Eq. (38), the operator $(\hat{H}-\hat{\mathcal{P}})$ annihilates states $|\mathrm{n}\rangle$ of improper symmetry with respect to the exchange of all pairs of electrons, while the states of proper symmetry satisfy the Schrödinger-like equation.

B. Approximations

Since it is difficult to obtain the exact form of PEO for multi-electron systems, we describe here several possible approximations of $\hat{\mathcal{P}}$. The natural approximation to $\hat{\mathcal{P}}$ is the truncation of an infinite series in Eqs. (31), (A5), and (A6) to a large but finite number of terms. Then a high-order differential equation that can be solved by standard methods is obtained. Attention should be paid to the domain of series convergence in Eqs. (31), (A5), and (A6). An alternative expression for the permutation operator is given in Ref. [19].

In the second approach we may approximate in Eq. (36) the exact operator $\prod_{i=1,j>i}^{k}\hat{\chi}_{ij}$ by a simpler one using results from the previous section. Consider the four-electron case, the function $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_4)$, and disregard the electrons' spins. Let us introduce two pairs of center-of-mass and relative-motion coordinates, see Eq. (3). Then we can obtain a set of functions in the form

$$\Psi_{ij,kl}(\boldsymbol{R}_{ij},\boldsymbol{r}_{ij},\boldsymbol{R}_{kl},\boldsymbol{r}_{kl}),\quad 1\leqslant i,j,k,l\leqslant 4, \tag{39}$$

and each of them satisfies Eq. (29) with PEO similar to that in Eq. (28) for appropriate pairs of coordinates. Each of the functions in Eq. (39) is symmetric or antisymmetric in two pairs of variables (instead of all pairs), but having all sets of function $\Psi_{ij,kl}$ the true function Ψ may be approximated.

In the third approximation we replace the exact Hamiltonian $\hat{H}$ entering to PEO in Eq. (38) by a simpler one $\hat{H}_0$, as, e.g., that of $k\geqslant 2$ free electrons in a harmonic potential. Let $|\Psi\rangle$ be the k-electron state and $\hat{\mathcal{P}}_0$ be the PEO corresponding to $\hat{H}_0$. Then we have

$$(\hat{H}-\hat{\mathcal{P}})|\Psi\rangle\simeq(\hat{H}-\hat{\mathcal{P}}_0)|\Psi\rangle. \tag{40}$$

Using Eq. (37) we find

$$(\hat{H}-\hat{\mathcal{P}})|\Psi\rangle\simeq\hat{H}|\Psi\rangle-\lambda\left(\sum_{\mathrm{n}_0^a}E_{\mathrm{n}_0^a}\big|\mathrm{n}_0^a\big\rangle\big\langle\mathrm{n}_0^a\big|\right)|\Psi\rangle=E|\Psi\rangle, \tag{41}$$

where λ is a parameter, $|\mathrm{n}_0^a\rangle$ are the antisymmetric states of $\hat{H}_0$ with respect to the exchange of all pairs of electrons, and $E_{\mathrm{n}_0^a}$ are the corresponding energies. The summation in Eq. (41) is restricted to a finite number of states. The presence of λ in Eq. (41) allows us to switch on the approximate PEO to the Schrödinger equation. If the obtained function Ψ has proper symmetry with respect to the exchange of all pairs of electrons then both Ψ and the corresponding energy E weakly depend on λ since, in this case, the second term in Eq. (41) vanishes or is small. If the calculated function Ψ has improper symmetry, then both Ψ and E strongly depend on λ because, in this case, the second term in Eq. (41) is large and it strongly influences Ψ and E. The described approach gives a practical method of finding multi-electron states having proper symmetry with respect to the exchange of all pairs of electrons. An example of such calculations for Hooke's atom is shown in the next section.

A possible generalization of Eq. (41) is to treat the second term in this equation as a kernel operator that ensures the antisymmetry of the resulting function Ψ for some set of states, e.g., low-energy ones. Let $|\boldsymbol{Q}\rangle=|\boldsymbol{r}_1,\dots,\boldsymbol{r}_k\rangle$ and $\Psi(\boldsymbol{Q})=\Psi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_k)$. Then we have from Eq. (41)

$$\begin{aligned}\langle\boldsymbol{Q}|\hat{H}-\hat{\mathcal{P}}|\Psi\rangle&\simeq\hat{H}\Psi(\boldsymbol{Q})-\lambda\int\hat{K}(\boldsymbol{Q}',\boldsymbol{Q})\Psi(\boldsymbol{Q}')d\boldsymbol{Q}'\\&=E\Psi(\boldsymbol{Q}).\end{aligned} \tag{42}$$

Comparing Eqs. (41) and (42) we find

$$\hat{K}(\boldsymbol{Q},\boldsymbol{Q}')=\sum_{\mathrm{n}_0^a}E_{\mathrm{n}_0^a}\big\langle\boldsymbol{Q}\big|\mathrm{n}_0^a\big\rangle\big\langle\mathrm{n}_0^a\big|\boldsymbol{Q}'\big\rangle. \tag{43}$$

The idea of the kernel approach is that $\hat{K}(\boldsymbol{Q},\boldsymbol{Q}')$ in Eq. (42) can be any mathematical operator without physical meaning. As an example, when in Eq. (43) the energies $E_{\mathrm{n}_0^a}$ are replaced by a constant value $\mathcal{E}_c$ and the summation limited to $\mathrm{n}_{\max}$ terms, the simpler expression

$$\hat{K}_1(\boldsymbol{Q},\boldsymbol{Q}')=\mathcal{E}_c\sum_{\mathrm{n}_0^a}^{\mathrm{n}_{\max}}\big\langle\boldsymbol{Q}\big|\mathrm{n}_0^a\big\rangle\big\langle\mathrm{n}_0^a\big|\boldsymbol{Q}'\big\rangle \tag{44}$$

is obtained, which also selects states having proper symmetry with respect to the exchange of all pairs of electrons. However, the kernel in Eq. (44) works correctly only for states having similar energies to those corresponding to functions $\langle \boldsymbol{Q}|\mathrm{n}_0^a\rangle$ in Eq. (44). The example of the kernel approach to Hooke's atom is given in the next section.

Finally, we discuss the approximation in which the expected value of $(\hat{H} - \hat{\mathcal{P}})$ over a trial function $|\Phi^a\rangle$ that is already antisymmetric with respect to the exchange of all pairs of electrons is calculated. Assuming that $\langle \Phi^a|\Phi^a\rangle = 1$ we can obtain from Eq. (37)

$$\langle \Phi^a|\hat{\mathcal{P}}|\Phi^a\rangle = 0, \tag{45}$$

since in this case the trial functions $|\Phi^a\rangle$ are a linear combination of states $|\mathrm{n}^a\rangle$ that are antisymmetric with respect to the exchange of all pairs of electrons, while $\hat{\mathcal{P}}$ does not include these states in its spectral resolution, see Eq. (37). Then

$$\langle \Phi^a|\hat{H} - \hat{\mathcal{P}}|\Phi^a\rangle \equiv \langle \Phi^a|\hat{H}|\Phi^a\rangle = E_a, \tag{46}$$

where E_a is approximated energy. A practical consequence of Eqs. (45) and (46) is that, when energies and states of the multi-electron system with the trial function in the form of Slater determinant are calulated variationally, then the PEO identically vanishes and there is no need to introduce it to the calculations.

IV. EXAMPLES OF $\hat{P}$ OPERATORS FOR HOOKE'S ATOM

Here we show two examples of $\hat{P}$ for two-electron systems and rederive analytically or numerically the results of Eqs. (26) to (28) by explicit summations over even or odd states of the Hamiltonian spectrum, see Eqs. (9) and (10).

We consider first the Hooke's atom in 2D whose Hamiltonian is given in Eq. (2) with $U(\boldsymbol{r}_i) = kr_i^2/2$ and $i = 1, 2$, where $k > 0$ is the harmonic potential strength [11–15]. Then $\hat{H}$ separates into two parts $\hat{H}_{\boldsymbol{R}}$ and $\hat{H}_{\boldsymbol{r}}$ depending on $\boldsymbol{R}$ and $\boldsymbol{r}$, respectively. The eigenfunctions of $\hat{H}$ are $\Psi(\boldsymbol{R}, \boldsymbol{r}) = F(\boldsymbol{R})f(\boldsymbol{r})$, where $F(\boldsymbol{R})$ and $f(\boldsymbol{r})$ satisfy equations

$$\left(-\frac{1}{4}\nabla_{\boldsymbol{R}}^2 + kR^2\right)F(\boldsymbol{R}) = E_R F(\boldsymbol{R}), \tag{47}$$

$$\left(-\nabla_{\boldsymbol{r}}^2 + \frac{1}{r} + \frac{1}{4}kr^2\right)f_{m,n}(\boldsymbol{r}) = E_{m,n}f_{m,n}(\boldsymbol{r}), \tag{48}$$

where $E_{m,n}$ is the energy of nth state with the angular momentum number m. The center-of-mass motion, as given in Eq. (47), is described by the 2D harmonic oscillator. For the relative motion in Eq. (48) we set: $f_{m,n}(\boldsymbol{r}) = g_{m,n}(r)e^{im\phi}/\sqrt{2\pi}$, where $g_{m,n}(r)$ are solutions of

$$\left(-\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{m^2}{r^2} + \frac{1}{r} + \frac{k}{4}r^2\right)g_{m,n}(r) = E_{m,n}g_{m,n}(r). \tag{49}$$

Consider the operator $\hat{P}^o$ in Eq. (10). Since $\hat{H}_{\boldsymbol{R}}$ in Eq. (47) is not affected by $\hat{P}^o$ we concentrate on $\hat{H}_{\boldsymbol{r}}$. Let $|m, n\rangle$ be an eigenstate of Eq. (48), and $\langle \boldsymbol{r}|m, n\rangle = f(\boldsymbol{r})$. Then we have

$$\begin{aligned}\hat{P}^o &= \sum_{m=-\infty}^{\infty}\sum_{n=1}^{\infty} E_{2m+1,n}|2m+1, n\rangle\langle 2m+1, n| \\ &= \hat{H}\left(\sum_{m=-\infty}^{\infty}\sum_{n=1}^{\infty}|2m+1, n\rangle\langle 2m+1, n|\right).\end{aligned} \tag{50}$$

In the position representation there is

$$\begin{aligned}\langle \boldsymbol{r}|\hat{P}^o|\boldsymbol{r}'\rangle &= \frac{1}{2\pi}\int d^2\boldsymbol{r}''\langle \boldsymbol{r}|\hat{H}|\boldsymbol{r}''\rangle \sum_{m=-\infty}^{\infty} e^{i(2m+1)(\phi''-\phi')} \\ &\quad \times \sum_{n=1}^{\infty} g_{2m+1,n}(r'')^* g_{2m+1,n}(r').\end{aligned} \tag{51}$$

We first calculate the sum over n. The functions $g_{m,n}(r)$ are normalized using the weight function $w_g(r) = r$. Consider functions $h_{m,n}(r) = \sqrt{r}g_{m,n}(r)$ normalized using the weight function $w_h(r) = 1$. They are eigenfunctions of the equation, see Eq. (49),

$$\left(-\frac{d^2}{dr^2} + \frac{m^2 - 1/4}{r^2} + \frac{1}{r} + \frac{k}{4}r^2\right)h_{m,n}(r) = E_{m,n}h_{m,n}(r). \tag{52}$$

For fixed m, functions $h_{m,n}(r)$ form a complete set of states of the Hermitian operator in Eq. (49), so there is

$$\sum_{n=1}^{\infty} h_{2m+1,n}(r'')^* h_{2m+1,n}(r') = \delta(r' - r''), \tag{53}$$

which gives

$$\sum_{n=1}^{\infty} g_{2m+1,n}(r'')^* g_{2m+1,n}(r') = \frac{\delta(r' - r'')}{r''}, \tag{54}$$

and the result of the summation over n does not depend on m. Consider now the sum over m in Eq. (51). Let $\xi = \phi'' - \phi'$. Then we have

$$\frac{1}{2\pi}\sum_{m=-\infty}^{\infty} e^{i(2m+1)\xi} = \frac{e^{i\xi}}{2\pi}\sum_{m=-\infty}^{\infty} e^{im(2\xi)} = \frac{e^{i\xi}}{2}\delta(\xi - N\pi), \tag{55}$$

which gives $(\phi'' - \phi') = 0$ or $(\phi'' - \phi') = \pi$ since $(\phi' - \phi'') \in [0, 2\pi)$. In Eq. (55) we used the following identity: $\sum_{m=-\infty}^{\infty} e^{im\xi} = 2\pi\delta(\xi - 2N\pi)$ with N integer. Then we obtain

$$\begin{aligned}\langle \boldsymbol{r}|\hat{P}^o|\boldsymbol{r}'\rangle &= \int d^2\boldsymbol{r}''\langle \boldsymbol{r}|\hat{H}|\boldsymbol{r}''\rangle \\ &\quad \times \left[\frac{1}{2}\delta(\phi'' - \phi') + \frac{e^{i\pi}}{2}\delta(\phi'' - \phi' + \pi)\right] \\ &\quad \times \left[\frac{1}{r''}\delta(r'' - r')\right].\end{aligned} \tag{56}$$

There is $\langle \boldsymbol{r}|\hat{H}|\boldsymbol{r}''\rangle = \delta(\boldsymbol{r} - \boldsymbol{r}'')$ since the Hamiltonian is a local operator. Using the identity $\delta(\boldsymbol{r} - \boldsymbol{r}') = (1/r)\delta(r - r')\delta(\phi - \phi')$ for the 2D delta function Eq. (27) is obtained. The generalization of this approach to 1D and 3D Hooke's atoms is straightforward.

In the second example we calculate numerically the operator $\hat{P}^o$ in a system in which the functions $f(r, \phi)$ do not separate into products of two one-dimensional functions. Consider the model similar to the Hooke's atom in Eq. (49) but with a nonradial external potential. Its Hamiltonian is given by Eq. (2) with $U(\boldsymbol{r}_i) = k_x x_i^2/2 + k_y y_i^2/2$ and $i = 1, 2$. The potential strengths $k_x, k_y > 0$. Introducing center-of-mass and relative motion coordinates we obtain

$$\left(-\frac{1}{4}\nabla^2_{\boldsymbol{R}} + k_xX^2 + k_yY^2\right)F(\boldsymbol{R}) = E_RF(\boldsymbol{R}), \tag{57}$$

$$\left(-\frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} + \frac{1}{r} + \frac{1}{4}k_yr^2 + qr^2\cos(\phi)^2\right)f(\boldsymbol{r}) = E_rf(\boldsymbol{r}), \tag{58}$$

where $q = k_x - k_y$ characterizes the anisotropy of the external potential. To find $\hat{P}^o$ we expand functions $f(r,\phi)$ in Eq. (58) into the set of eigenstates $g_{m,n}(r)e^{im\phi}/\sqrt{2\pi}$ of the Hooke's atom, see Eq. (49),

$$f(r,\phi) = \sum_{m=-m_{\max}}^{m_{\max}} \sum_{n=1}^{n_{\max}} b_{m,n}g_{m,n}(r)e^{im\phi}, \tag{59}$$

where $b_{m,n}$ are the expansion coefficients, $m_{\max} = 16$ and $n_{\max} \simeq 250$. The presence of Hooke's atom functions in Eq. (49) ensures orthogonality of the basis. We used 8054 basis functions $g_{m,n}(r)$, which are calculated by the shooting method, see Appendix B. We introduce a mapping $(m,n) \rightarrow i$ which labels the basis functions $g_{m,n}(r)$ with a single index i.

The eigenenergies and eigenstates of the Hamiltonian in Eq. (58) are obtained by solving the problem of the finite-size matrix $\sum_{i'} H_{ii'}a_{i'} = Ea_i$, where a_i are uniquely obtained from $b_{m,n}$ by the mapping $i \rightarrow (m,n)$. Using the inverse mapping $(m,n) \rightarrow i$ we have

$$H_{ii'} = E_i\delta_{i,i'} + qc_{m,m'}\int_0^\infty [r^2g_{m,n}(r)g_{m',n'}(r)]rdr, \tag{60}$$

where for fixed m the functions $g_{m,n}$ are normalized $\int_0^\infty g_{m,n}(r)g_{m,n'}(r)rdr = \delta_{n,n'}$. The selection rules for ϕ integrals are

$$c_{m,m'} = \frac{1}{2\pi}\int_0^{2\pi} e^{i(m-m')\phi}\cos(\phi)^2d\phi = \frac{1}{2}\delta_{m,m'} + \frac{1}{4}\delta_{m,m'\pm 2}. \tag{61}$$

The nonzero elements of $H_{ii'}$ are those with $m' = m$ and $m' = m \pm 2$. Let $\{f_l^e(r,\phi)\}$ be a set of states of $H_{ii'}$ obtained from even functions $g_{2m,n}(r)e^{(2m)i\phi}/\sqrt{2\pi}$, and $\{f_l^o(r,\phi)\}$ be a set of states of $H_{ii'}$ obtained from odd functions $g_{2m+1,n}(r)e^{(2m+1)i\phi}/\sqrt{2\pi}$. Then

$$\hat{P}^\eta(\boldsymbol{r},\boldsymbol{r}') = \hat{H}(\boldsymbol{r},\boldsymbol{r})\,\mathcal{S}^\eta(\boldsymbol{r},\boldsymbol{r}'), \tag{62}$$

where

$$\mathcal{S}^\eta(\boldsymbol{r},\boldsymbol{r}') = \sum_l f_l^\eta(r,\phi)^* f_l^\eta(r',\phi'), \tag{63}$$

and $\eta \in \{e,o\}$. Note that for $l \rightarrow \infty$ there is $\mathcal{S}^e(\boldsymbol{r},\boldsymbol{r}') + \mathcal{S}^o(\boldsymbol{r},\boldsymbol{r}') \rightarrow \delta(\boldsymbol{r},\boldsymbol{r}')$. In our calculations we take 4146 $f_l^e(r,\phi)$ functions and 3908 $f_l^o(r,\phi)$ functions, respectively.

In Fig. 1 we plot the sums $\mathcal{S}^\eta(\boldsymbol{r},\boldsymbol{r}')$ in Eq. (63) for $\boldsymbol{r}' = \mathbf{1}$ and several $(\phi - \phi')$ values, where $\mathbf{1}$ is a unit vector in arbitrary direction. In our calculations we take $k_y = 4$ and $k_x = 9.61$, which gives $q = 1.4025$, see Eq. (48). In Fig. 1(a) there is $(\phi - \phi') = 0$ and both sums $\mathcal{S}^\eta(\boldsymbol{r},\mathbf{1})$ tend to $\delta(r-1)$, where $r = |\boldsymbol{r}|$. We also plot the unnormalized function $g_{0,1}(r)$.

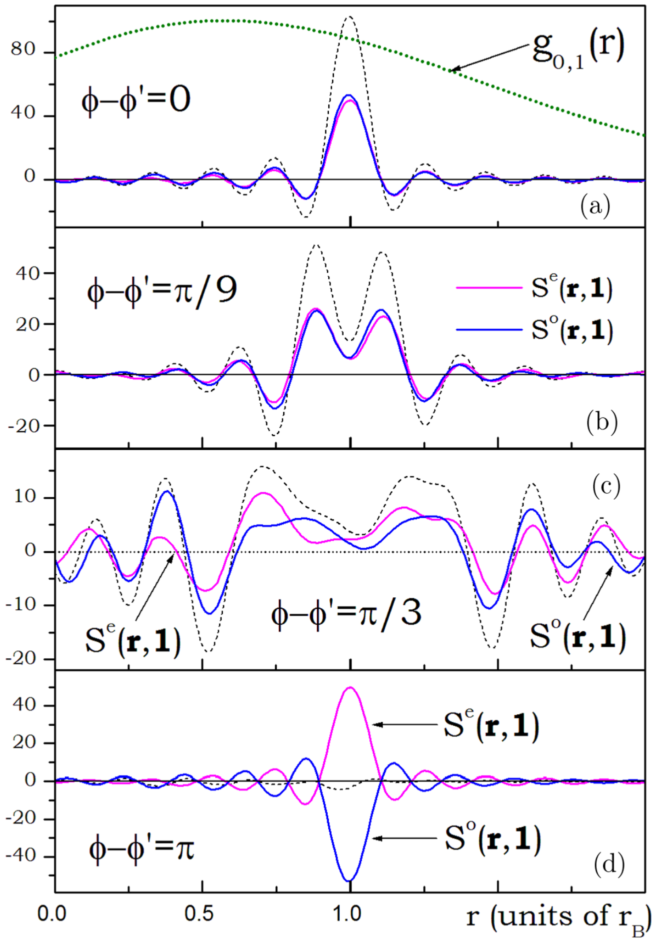

FIG. 1. Dimensionless sums $\mathcal{S}^o(\boldsymbol{r},\mathbf{1})$ and $\mathcal{S}^e(\boldsymbol{r},\mathbf{1})$ given in Eq. (63) calculated numerically for nonsymmetric two-dimensional Hooke's atom in Eq. (58) for several values of relative phases $(\phi - \phi')$. The dashed lines represent sums $\mathcal{S}^o(\boldsymbol{r},\mathbf{1}) + \mathcal{S}^e(\boldsymbol{r},\mathbf{1})$ approximating delta function $\delta(\boldsymbol{r}-\mathbf{1})$. In panel (a) the dotted line indicates ground-state function $g_{0,1}(r)$ of two-dimensional Hooke's atom in Eq. (48).

It is seen that $\mathcal{S}^\eta$ are more localized than $g_{0,1}(r)$ which justifies treating $\mathcal{S}^\eta(\boldsymbol{r},\mathbf{1})$ as approximations of the $\delta(r-1)$ function.

By increasing $(\phi - \phi')$ in Figs. 1(b) and 1(c) the sums $\mathcal{S}^\eta(\boldsymbol{r},\mathbf{1})$ gradually decrease, but they do not vanish because they are truncated to a finite number of terms. For $(\phi - \phi') = \pi$ in Fig. 1(d), the sum $\mathcal{S}^e(\boldsymbol{r},\mathbf{1})$ tends to $\delta(r-1)$, while the sum $\mathcal{S}^o(\boldsymbol{r},\mathbf{1})$ tends to $-\delta(r-1)$, so their sum practically cancels out (dotted line). The above results obtained numerically in Fig. 1 for a nonseparable function $f(r,\phi)$ illustrate the general formulas in Eqs. (26) to (28).

We emphasize two approximations related to Fig. 1. First, the summations over angular states are limited to $0 \leqslant m \leqslant 16$, and the results may be incomplete because we omitted basis functions with higher m. Second, for fixed m we take $n \simeq 250$ radial functions $g_{m,n}(r)$ and claim that they are sufficient to approximate combinations of delta functions in Eqs. (26) and (27). Both issues are clarified in Figs. 2 and 3.

In Fig. 2 we show normalized functions $g_{0,1}(r)$ (ground state), $g_{16,1}(r)$, and $g_{16,200}(r)$. As seen from Figs. 2(b) and 2(c), functions having $m = 16$ practically vanish at $r = 1$ and

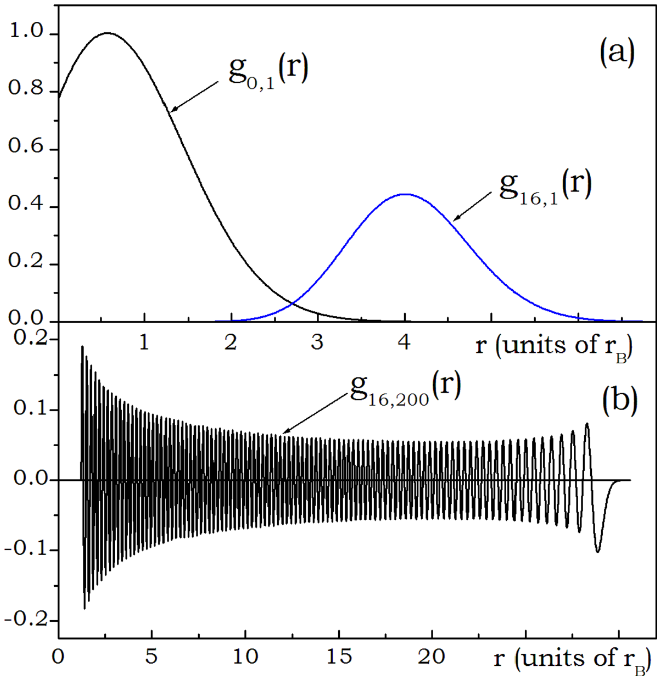

FIG. 2. Functions $g_{m,n}(r)$ of 2D Hooke's atom given in Eq. (49) calculated numerically for three m, n values. Function $g_{0,1}(r)$ corresponds to the ground state of the system.

they give negligible contributions to $\mathcal{S}^\eta(\boldsymbol{r},\mathbf{1})$ for $0 \leqslant r \leqslant 2$, see Eq. (63). This result confirms the validity of truncating the summation over m states to $m \leqslant 16$ in Fig. 1. Selecting larger r' and r one has to include states with larger m.

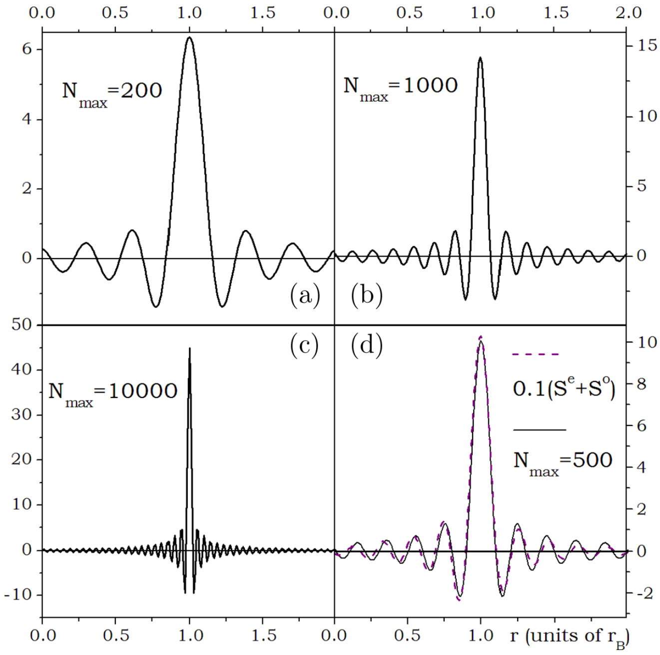

FIG. 3. (a)–(c) Dimensionless sums $S(x,x')$ given in Eq. (64) for 1D harmonic oscillator functions calculated numerically for four $N_{\max}$ values and $x' = 1$. (d) Sum $S(x,1)$ calculated for $N_{\max} = 500$ compared with rescaled sum $\mathcal{S}^e(\boldsymbol{r},\mathbf{1}) + \mathcal{S}^o(\boldsymbol{r},\mathbf{1})$ defined in Eq. (63) and shown in Fig. 1(a), dashed line. The scaling factor is $c = 0.1$.

To show that finite sums $\mathcal{S}^\eta$ in Fig. 1 approximate the combinations of delta functions we consider the set of functions $\{\psi_n(x)\}$ being states of the one-dimensional harmonic oscillator with the potential $U(x) = x^2$. Let

$$S(x,x') = \sum_{n}^{N_{\max}} \psi_n(x)\psi_n(x') \to \delta(x-x'). \tag{64}$$

We calculate $S(x,x')$ numerically using the recursion relation [20] $\sqrt{\frac{n+1}{2}}\psi_{n+1}(x) = x\psi_n(x) - \sqrt{\frac{n}{2}}\psi_{n-1}(x)$ with the initial conditions $\psi_0(x)=\pi^{-1/4}\exp(-x^2/2)$ and $\psi_{-1}(x)=0$. In Fig. 3 we show $S(x,1)$ for several values of $N_{\max}$. As seen in Figs. 3(a), 3(b) and 3(c), when increasing $N_{\max}$ the sums $S(x,1)$ tend to $\delta(x-1)$. In Fig. 3(d) we compare the sum $S(x,1)$ for $N_{\max} = 500$ with the rescaled sum $\mathcal{S}^e(\boldsymbol{r},\mathbf{1}) + \mathcal{S}^o(\boldsymbol{r},\mathbf{1})$ for $(\phi-\phi') = 0$ shown in Fig. 1(a). Both curves are close to each other up to a scaling factor $c = 0.1$, which confirms the delta-like character of the curves shown in Fig. 1.

As the third example we calculate the states and energies of the symmetric 2D Hooke's atom described in Eq. (49) with the use of Eqs. (41) and (42). We analyze odd states of $\hat{H}$, so we apply the $\hat{P}^o$ operator, see Eq. (10). In the position representation $|\boldsymbol{Q}\rangle = |\boldsymbol{R},\boldsymbol{r}\rangle$ Eqs. (41) and (42) read

$$\begin{aligned}
&\hat{H}\Psi(\boldsymbol{Q}) - \left(\hat{H}_0 - \hat{P}_0^o\right)\Psi(\boldsymbol{Q})\\
&\quad = \hat{H}\Psi(\boldsymbol{Q}) - \lambda\sum_{\mathrm{n}_0^e} E_{\mathrm{n}_0^e}\langle\boldsymbol{Q}|\mathrm{n}_0^e\rangle\int\langle\mathrm{n}_0^e|\boldsymbol{Q}'\rangle\Psi(\boldsymbol{Q}')d^2\boldsymbol{Q}'\\
&\quad = E\Psi(\boldsymbol{Q}),
\end{aligned}\tag{65}$$

and $\boldsymbol{R},\boldsymbol{r}$ are the center-of-mass and relative-motion coordinates, respectively. The superscript e in Eq. (65) denotes even states and energies of $\hat{H}_0$ since the odd ones were eliminated by $\hat{P}_0^o$. Let

$$\Psi(\boldsymbol{R},\boldsymbol{r}) = \frac{1}{\sqrt{2\pi}}F(\boldsymbol{R})g_{m,n}(r)e^{im\phi}, \tag{66}$$

$$\langle\boldsymbol{R},\boldsymbol{r}|\mathrm{n}_0^a\rangle = \frac{1}{\sqrt{2\pi}}F(\boldsymbol{R})\psi_{2j,l}(r)e^{2ij\phi}, \tag{67}$$

where $F(\boldsymbol{R})$ satisfies Eq. (47), $g_{m,n}(r)$ is the solution of Eq. (49), $\psi_{2j,l}(r)$ and $\epsilon_{2j,l}$ are functions and energies of the 2D harmonic oscillator, respectively, m, j describe angular momentum, and n, l label the discrete states. Functions $\psi(\boldsymbol{r}) = \psi_{2j,l}(r)e^{2ij\phi}$ in Eq. (67) are even: $\psi(\boldsymbol{r}) = \psi(-\boldsymbol{r})$. We approximate $\hat{\mathcal{P}}_0$ in Eq. (65) by restricting the summations to a few low-energy states $j = 0, \pm 1$ and $n = 0, 1, 2$. For a given m and n one has from Eq. (65)

$$\begin{aligned}
&\hat{H}_r g_{m,n}(r)\frac{e^{im\phi}}{\sqrt{2\pi}} - \lambda\sum_{l=0}^{2}\sum_{j=-1}^{1}\epsilon_{2j,l}\phi_{2j,l}(r)\frac{e^{2ij\phi}}{\sqrt{2\pi}}\\
&\quad\times\int_0^\infty \phi_{2j,l}(r')g_{m,n}(r')r'dr'\int_0^{2\pi}\frac{e^{i(m-2j)\phi'}}{2\pi}d\phi'\\
&\quad = E_{m,n}g_{m,n}(r)\frac{e^{im\phi}}{\sqrt{2\pi}},
\end{aligned}\tag{68}$$

where $\hat{H}_r$ is defined in Eq. (49) and we use $\int|F(\boldsymbol{R}')d^2\boldsymbol{R}'|^2=1$. The kernel corresponding to Eq. (68) is, see Eqs. (43)

and (44),

$$\hat{K}(\boldsymbol{r},\boldsymbol{r}') = \sum_{l=0}^{2}\sum_{j=-1}^{1} \epsilon_{2j,l}\phi_{2j,l}(r)\phi_{2j,l}(r')\frac{e^{2ij(\phi-\phi')}}{2\pi}. \tag{69}$$

Now we discuss solutions of Eq. (68) for various values of m and we analyze three cases: $m = \pm 1$, $m = 0, \pm 2$, and $|m| > 2$. Consider first two odd states with $m = \pm 1$. Since the second integral in Eq. (68) vanishes for $m = \pm 1$ we obtain

$$\hat{H}_r g_{m,n}(r) = E_{m,n} g_{m,n}(r), \tag{70}$$

i.e., Eq. (49). The solutions of Eq. (70) do not depend on λ. If in Eq. (68) one uses the kernel $\hat{K}_1(\boldsymbol{r},\boldsymbol{r}')$ of the form, see Eq. (44),

$$\hat{K}_1(\boldsymbol{r},\boldsymbol{r}') = \mathcal{E}_c \sum_{j=-1}^{1}\phi_{2j,0}(r)\phi_{2j,0}(r')\frac{e^{2ij(\phi-\phi')}}{2\pi}, \tag{71}$$

then for $g_{m,n}(r)$ one also obtains Eq. (70). In Eq. (71) the sum over l is limited to a single term with $l = 0$ and $\mathcal{E}_c$ is an arbitrary energy.

Consider now three even states with $m = 0, \pm 2$. Then the sum over j in Eq. (68) reduces to a single term with $2j = m$ and one has

$$\hat{H}_r g_{m,n}(r) - \lambda \sum_{l=0}^{2}\epsilon_{m,l}\phi_{m,l}(r)\int_0^\infty \phi_{m,l}(r')g_{m,n}(r')r'dr' \\ = E_{m,n}g_{m,n}(r). \tag{72}$$

Equation (72) is the differential-integral equation for unknown function $g_{m,n}(r)$, and it resembles Eq. (29). In Eq. (72) the function $g_{m,n}(r)$ does not vanish and it depends on λ. This also occurs when in Eq. (68) one replaces the kernel $\hat{K}(\boldsymbol{r},\boldsymbol{r}')$ by $\hat{K}_1(\boldsymbol{r},\boldsymbol{r}')$ in Eq. (71).

Consider now the exact operator $\hat{\mathcal{P}}$ instead of $\hat{\mathcal{P}}_0$. Then we set in Eq. (72) $\psi_{j,l}(r) \to g_{m,n}(r)$ and $\epsilon_{j,l} \to E_{m,n}$. For $m = 0, \pm 2$ we have

$$\hat{H}_r g_{m,n}(r) - \lambda E_{m,n}g_{m,n}(r) = E_{m,n}g_{m,n}(r). \tag{73}$$

For $\lambda = 1$ the left-hand side of Eq. (73) vanishes, which gives $g_{m,n}(r) \equiv 0$, as expected from Eq. (38) for the exact $\hat{\mathcal{P}}$ operator.

Finally, for $|m| > 2$ Eq. (70) is obtained both for odd and even m since the approximate PEO in Eq. (68) contains only states with angular momenta $|m| \leqslant 2$. This also occurs for kernel $\hat{K}_1(\boldsymbol{r},\boldsymbol{r}')$ in Eq. (71).

From the above results we reach the following conclusions. First, by a properly chosen set of $\langle \boldsymbol{Q}|\mathrm{n}_0^a\rangle$ states in Eqs. (41), (43), and (65) we can construct an approximate operator $\hat{\mathcal{P}}_0$ that does not alter odd (or even) states of the Hamiltonian and strongly affects the states of the opposite symmetry. Second, the use of simpler kernel in Eqs. (44) and (71) leads to qualitatively similar results to those obtained for the kernel in Eqs. (42) and (69). Third, the parameter λ can be used as a tool for distinguishing states having proper or improper symmetry with respect to the exchange of all pairs of electrons. Finally, if one uses an approximate kernel in Eqs. (44) or (71), then they work correctly for some states only, in the above example only for those with $|m| \leqslant 2$.

V. DISCUSSION

In this work we introduced the PEO that ensures the appropriate symmetry of multi-electron eigenstate, see Eqs. (7) and (8). For two-electron systems we showed three alternative representations of PEO. In Eqs. (9) and (10) we expressed PEO in terms of infinite sums over subsets of states belonging to the spectrum of the Hamiltonian. Using this method we calculated PEO for isotropic and anisotropic Hooke's atom.

For 2D two-electron systems it is possible to express $\hat{P}$ in a closed form in terms of momentum operators, see Eqs. (21) to (23). In the position representation $\hat{P}$ is a nonlocal operator, and the states of the two-electron Hamiltonian should be calculated from the nonlocal Yamaguchi equation rather than the Schrödinger equation, see Eqs. (28) and (29).

In two-electron systems the spectrum of the Hamiltonian contains only symmetric or antisymmetric states. This is not valid in multi-electron cases since, for the antisymmetric states, the solutions of the Schrödinger equation may be symmetric for the exchange of some pairs of electrons and antisymmetric for the others. Only the application of the Pauli exclusion principle selects states of $\hat{H}$ that are antisymmetric for the exchange of all pairs of electrons.

The PEO can be generalized for multi-electron systems and it can be defined in two alternative forms: either in terms of operators $\hat{\chi}_{ij}$ [(see Eq. (33)] or by spectral resolution, [see Eq. (36)]. The $\hat{\chi}_{ij}$ operators can be represented as a product of an infinite power series of position and momentum operators and electron spins. In this representation PEO depends on the product of $\hat{\chi}_{ij}$ for all pairs of electrons. In the second representation $\hat{\mathcal{P}}$ is an operator that includes all states and energies of the Hamiltonian except states being antisymmetric with respect to the exchange of all pairs of electrons. For two-electron systems both forms of PEO reduce to the results in Sec. II. Note that PEO cannot be represented in a closed form for more than two electrons.

Several approximate formulas for $\hat{\mathcal{P}}$ were proposed in Sec. III. The most promising ones for multi-electron systems are based on the approximate forms of $\hat{\mathcal{P}}_0$ calculated for simpler systems as, e.g., for a set of free electrons in the harmonic potential, see Eq. (41). Another possibility is to treat $\hat{\mathcal{P}}_0$ as a kernel operator that ensures antisymmetry of the calculated wave function, see Eq. (42). This kernel may be treated as a mathematical object without clear physical meaning. Calculated energies and states of the 2D Hooke's atom confirm the effectiveness of these approximations.

It is interesting to compare the results obtained with the use of PEO to variational methods for trial functions taken in the form of Slater determinants. As shown in Eq. (45), once the wave function $|\Psi^a\rangle$ is already antisymmetrized there is $\hat{\mathcal{P}}|\Psi^a\rangle = 0$, and it is not necessary to introduce PEO. Variational calculations with the use of trial function in the Slater form are the most common method of calculating the energies and states of multi-electron systems. In practice this method is the best compared to other approaches. The conclusion is that for variational calculations with the Slater determinants PEO is not needed.

However, if one goes beyond variational calculations or if a trial variational function is not antisymmetric in all pairs of electrons, then one encounters the problem of ensuring the antisymmetry of the multi-electron function. This problem could be solved either ex-post, by eliminating spurious solutions that are not antisymmetric with respect to the exchange of all pairs or electrons, or by adding PEO to the Hamiltonian that ensures antisymmetry of the resulting wave function. As pointed out above, it seems to be impossible to find the exact PEO for arbitrary systems, but the application of the approximate forms of PEO proposed in Sec. III may be sufficient to obtain a wave-function fulfilling antisymmetry requirement.

The fundamental difference between the PEO method and commonly used methods, as e.g., the configuration interaction (CI) method is as follows. In the PEO approach one does not take any assumption of the wave function, but the PEO ensures proper antisymmetry of the resulting wave function. Any additional operator is not introduced in the CI method, but the multi-electron wave function as a combination of Slater determinants is assumed. Therefore, the PEO method is, in some sense, "opposite" to the commonly used methods based on Slater determinants. In both approaches, if w takes the exact PEO or exact antisymmetric trial function then identical results are obtained. However, since, in practice, approximate methods are always used, as e.g., those in Sec. III, it may turn out that in some problems one method is superior to the other. As an example, for the 2D Hooke's atom the used PEO gives exact energies and states, see Eq. (70), but the variational method based on Slater determinants leads to approximate results.

In this work we concentrate on the analysis of the PEO for the 2D Hooke's atom, which is simpler than Hooke's atom in 3D. In the later case the Hamiltonian also separates into parts depending on the center-of-mass motion and the relative motion. The states of the Hooke's atom Hamiltonian in 3D have the form $\Psi(\boldsymbol{r}) = g_{l,n}(r)Y_{l,m}(\Theta,\phi)$, where $Y_{l,m}(\Theta,\phi)$ are the spherical harmonics in the standard notation. Functions $g_{l,m}(r)$ are the solutions of the equation

$$\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2} + \frac{1}{r} + \frac{k}{4}r^2\right)g_{l,n}(r) = E_{l,n}g_{l,n}(r), \tag{74}$$

where $l = 0, 1\ldots$ is the angular momentum number and $E_{l,n}$ are the energies. Functions $g_{l,n}(r)$ in Eq. (74) are similar to $g_{m,n}(r)$ in Eq. (49), see Fig. 2. In 3D the transformation $\boldsymbol{r} \to -\boldsymbol{r}$ does not change the $r = |\boldsymbol{r}|$ coordinate, but changes the angular functions

$$Y_{l,m}(\Theta,\phi) \to Y_{l,m}(\pi-\Theta,\phi+\pi) = (-1)^l Y_{l,m}(\Theta,\phi). \tag{75}$$

Then, similarly to the 2D case, the states with even l are symmetric with respect to the exchange of electrons, while those with odd l are asymmetric. In 3D one may *not* express $\hat{P}$ in terms of the differential operator because the transformation $\Theta \to \pi - \Theta$ cannot be expressed in terms of the translation operator, see Eqs. (14) and (23). However, the representation of PEO in Eqs. (26) to (28) is valid also in the 3D Hooke's atom model.

There exist two systems having two interacting electrons, i.e., the He atom and the Li ion. In these systems the external potential acting on the electrons is the Coulomb potential of the nucleus. The Schrödinger equations of both systems do not separate into the center-of-mass and relative motions, and to find eigenvalues or the eigenstates one has to use approximate methods, e.g., variational calculations, molecular orbital approximations, or perturbation methods [6,7]. These methods work correctly for low-energy states but their accuracy decreases for high energies. For this reason it is practically impossible to calculate the PEO for the He atom and Li ion by summating the eigenstates in Eqs. (9) and (10). However, the results in Figs. 1 and 3 suggest that for both systems the position representation of PEO is also given in Eqs. (26) to (28). Note, that for the 3D He atom with the $L = 0$ the motion of electrons and nucleus is confined to a plane fixed in configuration space, see the review article in Ref. [7]. In this case the PEO is given by Eq. (23), as well as for the hypothetical 2D He atom.

Let us briefly discuss some issues related to the spin part of the wave function for multi-electron systems. Consider first the three-electron case as, e.g., the Li atom and assume that the Hamiltonian of the system does not depend on electron spins. In such a case the wave function of the system is a product of the position-dependent and spin-dependent functions. For three spins there is 2^3 spins- combination, and they form four quartets and four doublets [21]. The quartet states are symmetric with respect to the exchange of the three pairs of spins, but the doublets are not, so to ensure proper symmetry of the three-electron wave function a combination of doublets should be taken. For the k-electron system there is 2^k spins combination, and for large k it is practically impossible to treat spins exactly, so one may either treat them classically or apply further approximations.

In Sec. II we assumed a spin-independent two-body Hamiltonian. In real systems one often meets spin-dependent interactions, usually related to the spin-orbit (SO) coupling. In practical realizations of Hooke's-like systems in quantum dots the SO is common, see Refs. [22–24]. In the standard notation there is $\hat{H}_{\text{SO}} = \alpha\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$. Then, for $L > 0$ the wave functions of electrons do not separate in position-only and spin-only parts and we may not use the approach in Sec. II. The general formalism in Sec. III as well as the approximate methods are valid also for systems with spin-dependent interactions including SO.

For the two-electron systems in Sec. II the PEO is defined as an operator that removes even or odd states from the Hamiltonian spectrum. Then the function $|\Psi\rangle$, being the solution of $(\hat{H}-\hat{P})|\Psi\rangle = E|\Psi\rangle$, includes odd or even states only. For the multi-electron systems in Sec. III the PEO is defined as an operator that removes antisymmetric states with respect to the exchange of all pairs of electrons from the Hamiltonian spectrum. Then the function $|\Psi\rangle$, being the solution of $(\hat{H}-\hat{\mathcal{P}})|\Psi\rangle = E|\Psi\rangle$, includes antisymmetric states only. The difference between both definitions is that even or odd states of the two-electron system relate to the relative motion of electrons, while for multi-electron systems the antisymmetry relates to the exchange of two electrons including their positions and spins.

PEO in the literature appear previously in calculations of nuclear matter properties [8–10]. In the approach of the authors of Ref. [10], the $\hat{G}$ matrix satisfies the Bethe-Goldstone equation

$$\hat{G} = v + v\frac{\hat{Q}}{\epsilon}\hat{G}, \tag{76}$$

where $\hat{G}$ is the reaction matrix, v is the two-nucleon interaction, ϵ is re-scaled energy, and $\hat{Q}$ is PEO in nuclear matter which prevents two particles from scattering into intermediate states with momenta below the Fermi energy. In some aspects this approach is similar to ours since the authors introduced an operator responsible for the Pauli exclusion principle, but PEO in the previous approach excluded some states from real or virtual scattering. In our approach PEO ensures proper symmetry of the multi-electron wave function.

VI. SUMMARY

In this work we introduce the PEO which ensures proper symmetry of the states of multi-electron systems with respect to the exchange of each pair of electrons. Once PEO is added to the Hamiltonian, no additional constraints due to the Pauli exclusion principle need to be imposed to the multi-electron wave function. PEO is analyzed for the two-electron Hamiltonian and we found its three representations. We concentrated on PEO in 2D in which it can be expressed in a closed form. Some properties of PEO in 3D and 1D for two-electron states are discussed. PEO are calculated analytically or numerically for symmetric and antisymmetric Hooke's atoms. We generalized PEO for multi-electron systems; its two alternative forms are obtained. Several approximations of PEO to multi-electron systems were derived. Kernel-based methods were proposed, and they seem to be the most promising approximations of PEO for practical calculations. It is shown that once the wave function $|\Psi^a\rangle$ is already antisymmetric with respect to the exchange of all pairs of electrons, $\hat{\mathcal{P}}|\Psi^a\rangle$ identically vanishes. For this reason, in variational calculations employing trial functions in the form of Slater determinants there is no need to introduce PEO. However, if we go beyond the variational calculations, we should introduce PEO to ensure antisymmetry of the resulting wave functions. We believe that the approach based on exact, approximate, or kernel forms of PEO may be useful in calculating energies and states of multi-electron systems.

APPENDIX A: AUXILIARY IDENTITIES

The spin-exchange operator $\hat{\Sigma}_{ij}$ is defined by its action on four two-spin states

$$\hat{\Sigma}_{ij}|\uparrow\uparrow\rangle = |\uparrow\uparrow\rangle, \tag{A1}$$

$$\hat{\Sigma}_{ij}|\uparrow\downarrow\rangle = |\downarrow\uparrow\rangle, \tag{A2}$$

$$\hat{\Sigma}_{ij}|\downarrow\uparrow\rangle = |\uparrow\downarrow\rangle, \tag{A3}$$

$$\hat{\Sigma}_{ij}|\downarrow\downarrow\rangle = |\downarrow\downarrow\rangle. \tag{A4}$$

Operator $\hat{\Sigma}_{ij}$ in Eq. (32) satisfies all of the above equations.

In 3D the particle exchange operator is given in Eq. (23) of Ref. [18] and for completeness we quote this expression

$$\begin{aligned}\hat{\Pi}_{ij} = &\sum_{n=0}^{\infty}\left(\frac{1}{n!}\right)\left(\frac{i}{\hbar}\right)^n\sum_{l=0}^{n}\sum_{m=0}^{l}\binom{n}{l}\binom{l}{m}\\ &\times(\hat{p}_{jx}-\hat{p}_{ix})^{n-l}(\hat{r}_{jx}-\hat{r}_{ix})^{n-l}\\ &\times(\hat{p}_{jy}-\hat{p}_{iy})^{l-m}(\hat{r}_{jy}-\hat{r}_{iy})^{l-m}\\ &\times(\hat{p}_{jz}-\hat{p}_{iz})^{m}(\hat{r}_{jz}-\hat{r}_{iz})^{m}.\end{aligned} \tag{A5}$$

By taking limit $\Delta\hat{x}_{ij} \to 0$ in Eq. (A5) one obtains the particle exchange operator in 2D

$$\begin{aligned}\hat{\Pi}_{ij} = &\sum_{n=0}^{\infty}\left(\frac{1}{n!}\right)\left(\frac{i}{\hbar}\right)^n\sum_{l=0}^{n}\binom{n}{l}(\hat{p}_{jx}-\hat{p}_{ix})^{n-l}(\hat{r}_{jx}-\hat{r}_{ix})^{n-l}\\ &\times(\hat{p}_{jy}-\hat{p}_{iy})^{l}(\hat{r}_{jy}-\hat{r}_{iy})^{l}.\end{aligned} \tag{A6}$$

Alternative expressions for $\hat{\Pi}_{ij}$ are given in Ref. [19].

APPENDIX B: SHOOTING METHOD

The eigenenergies and eigenstates of Hooke's atom in Eq. (49) are found using the shooting method [25]. As the initial guesses for the energies we use those of the two-dimensional harmonic oscillator equal to $E_n = \sqrt{(k/4)}(2n+1)$, $n = 0, 1, \ldots m$ and $k = 4$. Then we iteratively bracket the true energies of $\hat{H}$ by analyzing the behavior of $g_{m,n}(r)$ at large r. The advantage of the shooting method is that it is equally accurate for low- and high-energy states. Only functions with $m \geqslant 0$ were calculated since $g_{-m,n}(r) = g_{m,n}(r)$. We tabulate the normalized states of Eq. (49) from $n = 1$ (ground state) to $n = 250$ and from $m = 0$ to $m = 16$.

We solve Eq. (49) using the DVERK procedure which is the sixth-order Runge-Kutta method [26,27]. The accuracy of the calculations has been verified by checking the orthogonality of all pairs of $g_{m,n}(r)$ and $g_{m',n'}(r)$ functions with $m = m'$ and $n \neq n'$. In each case the accuracy below 10^{-5} has been obtained.

For small r there is $g_{0,n}(r) \simeq c_0(1+r)$ with $c_0 > 0$, and the initial conditions for the DVERK procedure are $g_{0,n}(0) = 1$, $g'_{0,n}(0) = h$, where h is the integration step, and $h \simeq 0.001 - 0.01\ \mathrm{r}_B$. For $m > 0$ and small r there is $g_{m,n}(r) \propto r^m$, and the initial conditions for the DVERK procedure are $g_{m,n}(0) = 0$, $g'_{m,n}(0) = mh^{m-1}$. For large m the last condition is unstable numerically, and it is replaced by $g_{m,n}(r_0) = g_c$, $g'_{m,n}(r_0) = mg_c/r_0$, $g_c \simeq 10^{-5}$, and $g_{m,n}(r) = 0$ for $r < r_0$. Here $r_0 > 0$ and its values for $g_{m,n}(r)$ are obtained by analysis of $g_{m-1,n}(r)$ for small r. Generally, r_0 gradually increases with m.

[1] G. W. Kellner, Z. Phys. **44**, 91 (1927).
[2] E. A. Hylleraas, Z. Phys. **48**, 469 (1928).
[3] E. A. Hylleraas, Z. Phys. **54**, 347 (1929).
[4] W. Pauli, Zeits. Phys. **31**, 765 (1925).

[5] W. Pauli, Phys. Rev. **58**, 716 (1940).
[6] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1957).
[7] G. Tanner, K. Richter, and J. M. Rost, Rev. Mod. Phys. **72**, 497 (2000).
[8] T. Cheon and E. F. Redish, Phys. Rev. C **39**, 331 (1989).
[9] E. Schiller, H. Muther, and P. Czerski, Phys. Rev. C **59**, 2934 (1999); **60**, 059901(E) (1999).
[10] K. Suzuki, R. Okamoto, M. Kohno, and S. Nagata, Nucl. Phys. A **665**, 92 (2000).
[11] S. Kais, D. R. Herschbach, and R. D. Levine, J. Chem. Phys. **91**, 7791 (1989).
[12] M. Taut, Phys. Rev. A **48**, 3561 (1993).
[13] M. Taut, J. Phys. A **27**, 1045 (1994).
[14] D. P. O'Neill and P. M. W. Gill, Phys. Rev. A **68**, 022505 (2003).
[15] https://en.wikipedia.org/wiki/Hooke%27s_atom.
[16] https://en.wikipedia.org/wiki/Translation_operator_(quantum_mechanics).
[17] Y. Yamaguchi, Phys. Rev. **95**, 1628 (1954).
[18] B. Schmid, Am. J. Phys. **47**, 166 (1979).
[19] D. Grau, Am. J. Phys. **49**, 669 (1981).
[20] https://en.wikipedia.org/wiki/Hermite_polynomials.
[21] A. L. Buchachenko and V. L. Berdinsky, Chem. Rev. **102**, 603 (2002).
[22] T. Darnhofer and U. Rossler, Phys. Rev. B **47**, 16020 (1993).
[23] L. Jacak, J. Krasnyj, and A. Wojs, Physica B **229**, 279 (1997).
[24] A. Poszwa, Act. Phys. Pol. A **138**, 477 (2020).
[25] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes: The Art of Scientific Computing*, 3rd ed. (Cambridge University Press, New York, 2007), Sec. 18.1.
[26] J. H. Verner, SIAM J. Num. Analysis **16**, 857 (1979).
[27] E. Hairer, S. P. Norsett, and G. Wanner, *Solving Ordinary Differential Equations I, Nonstiff Problems*, 2nd ed. (Springer Series in Computational Mathematics, Berlin, 1993), p. 181, Table 5.4.