Density functional theory is usually formulated in terms of the density in configuration space. Functionals of the momentum-space density have also been studied, and yet other densities could be considered. We offer a unified view from a second-quantized perspective and introduce a version of density functional theory that treats all single-particle contributions to the energy exactly. An appendix deals with semiclassical eigenvalues.

1. Introduction

The very rich literature on density functional theory (DFT) consists almost exclusively of articles on functionals of the configuration-space density and their many applications; see Refs. [1,2] and the references therein. There are, however, experimentally accessible properties of many-electron systems that require knowledge of the density in momentum space for their computation — the prime example are Compton profiles, the observed wavelength distribution of photons scattered off electrons with a range of initial velocities [3]. This triggered interest in an alternative version of DFT in terms of the momentum-space density which produced a handful of publications [4–9]. Perhaps it is worth considering functionals of yet other densities?

We present a unified view based on the second-quantized formalism for many interacting identical particles. The modes to which the cre-
ation and annihilation operators refer determine the natural choice of the single-particle density, and we obtain the functionals of this density by a constrained-search strategy of the Levy–Lieb kind \cite{10, 11}. We recover the familiar functionals of the configuration-space and the momentum-space densities and show how one can construct functionals of a third kind where all single-particle contributions to the energy have an exactly known functional while, as always, the functional for the contribution of the pair interaction requires systematic approximations.

An appendix offers remarks on semiclassical approximations. In particular, the familiar expressions for approximate WKB energies emerge without reference to wave functions.

### 2. Constrained search

We consider systems of many identical particles with pair interactions, for which the many-particle Hamilton operator $H_{\text{mp}}$ is the sum of single-particle contributions and pair contributions,

$$H_{\text{mp}} = H_{\text{single}} + H_{\text{pair}},$$

with

$$H_{\text{single}} = \sum_{a,a'} \psi(a)^\dagger \langle a| H_{1p} | a' \rangle \psi(a')$$

and

$$H_{\text{pair}} = \frac{1}{2} \sum_{a,a', b,b'} \psi(a)^\dagger \psi(b)^\dagger \langle a, b| H_{\text{int}} | a', b' \rangle \psi(b') \psi(a').$$

Here, $\psi(a)$ and $\psi(a)^\dagger$ are the annihilation and creation operators for the mode labeled by $a$, $|a\rangle$ is the single-particle ket for the $a$th mode, $\langle a| = |a\rangle^\dagger$ is the adjoint bra, and $\langle a, b| = |a, b\rangle = |a\rangle \otimes |b\rangle$ is a two-particle tensor-product ket; see, for example, Chapter 10 in Ref. \cite{12}. The modes refer to a complete orthonormal set in the single-particle space,

$$\langle a|b\rangle = \delta(a, b), \quad \sum_a |a\rangle \langle a| = 1,$$

where

$$\delta(a, b) = \begin{cases} 1 & \text{if } a = b \\ 0 & \text{if } a \neq b \end{cases} = \delta_{a,b}$$
Energy functionals of single-particle densities: A unified view

is the Kronecker delta symbol. While Eqs. (2.1)–(2.3) apply to systems of fermions or bosons, with the respective algebraic properties of the $\psi(a)$s and their adjoints, we focus on spin-$\frac{1}{2}$ fermions here and, therefore, have the anticommutators

$$
\psi(a)\psi(b) + \psi(b)\psi(a) = 0,
\psi(a)\psi(b) + \psi(b)\psi(a) = 0,
\psi(a)\psi(b) + \psi(b)\psi(a) = \delta(a,b).
$$

For the purpose of this paper, the generic form of the single-particle energy

$$
H_{1p}(\mathbf{R}, \mathbf{P}) = \frac{1}{2m} \mathbf{P}^2 + V_{\text{trap}}(\mathbf{R})
$$

is the sum of the kinetic energy and the potential energy associated with the conservative trapping forces; $\mathbf{P}$ and $\mathbf{R}$ are the momentum and position vector operators of a particle with mass $m$. Further, we only consider pair interaction energies that result from conservative line-of-sight forces,

$$
H_{\text{int}} = V_{\text{int}}(|\mathbf{R}_1 - \mathbf{R}_2|),
$$

where $\mathbf{R}_1$ and $\mathbf{R}_2$ are the position operators of any two particles. These restrictions can be lifted as the need arises. In particular, one can account for spin-dependent contributions, such as those of magnetic dipole-dipole interaction \[13, 14\], or one can replace $H_{\text{single}}$ of Eq. (2.2) with $H_{1p}$ of Eq. (2.7) by Dirac’s expression for relativistic fermions \[15\]. Of course, one can also generalize to systems with particles of two or more kinds.

We choose the second-quantized version of the Hamilton operator in Eqs. (2.1)–(2.3) because it is more flexible than the first-quantized version with

$$
H_{\text{single}} = \sum_{k=1}^{N} \left( \frac{1}{2m} P_k^2 + V_{\text{trap}}(\mathbf{R}_k) \right)
$$

and

$$
H_{\text{pair}} = \frac{1}{2} \sum_{j,k=1}^{N} V_{\text{int}}(|\mathbf{R}_j - \mathbf{R}_k|).
$$

\[The mode label could be continuous rather than discrete, or a combination of a continuous and a discrete label (position and spin, say), and then integrals replace the sums in Eqs. (2.2) and (2.3), and Dirac’s delta function replaces the Kronecker delta symbol. We leave these matters implicit until we need to be explicit about them.\]
In Eqs. (2.9) and (2.10), we have exactly $N$ particles; for Eqs. (2.2) and (2.3) this corresponds to only considering many-particle states from one eigenvalue sector of the number operator
\[ N = \sum_a \psi(a)\dagger \psi(a), \quad (2.11) \]
that is
\[ N\rangle = \{\rangle N \text{ for all permissible many-particle kets } \rangle. \quad (2.12) \]
The permissible kets are superpositions of the basic $N$-particle kets in the Fock space,
\[ \psi(a_1)\dagger \psi(a_2)\dagger \cdots \psi(a_N)\dagger \rangle\text{vac}, \quad (2.13) \]
where $N$ creation operators act on the vacuum ket $\rangle\text{vac}$, which describes the situation of no particles at all: $\psi(a)\langle\text{vac} = 0$ for all modes, $N\langle\text{vac} = 0$.

We exploit the flexibility of the second-quantized formulation by minimizing the energy under the constraint of a prechosen expectation value of $N$,
\[ \text{tr}(N\rho) = N \text{ for all permissible many-particle statistical operators } \rho, \quad (2.14) \]
where $N$ is now any positive number, integer or noninteger. As always, the requirements $\rho \geq 0$ and $\text{tr}(\rho) = 1$ identify the set of statistical operators. Other than that, the $\rho$s are linear combinations of the basic building blocks,
\[ \psi(a_1)\dagger \psi(a_2)\dagger \cdots \psi(a_K)\dagger \langle\text{vac}\rangle\psi(b_1)\psi(b_2)\cdots \psi(b_L), \quad (2.15) \]
with $K$ creation operators acting on the vacuum ket and $L$ annihilation operators acting on the vacuum bra $\langle\text{vac} | = |\text{vac}\rangle$.

We have
\[ |\text{vac}\rangle\langle\text{vac} = \prod_a \psi(a)\psi(a)\dagger \quad (2.16) \]
in view of the commutation relations in Eq. (2.6). Only terms in $\rho$ with $K = L$ contribute to the expectation value of $N$ in Eq. (2.14) and that of $H_{\text{mp}}$ in
\[ E_{\text{gs}}(N) = \min_{\rho} \{\text{tr}(H_{\text{mp}}\rho)\}, \quad (2.17) \]
where $H_{mp}$ is the Hamilton operator of Eqs. (2.1)–(2.3), and only $\rho$'s that obey the constraint in Eq. (2.14) participate in the competition. As indicated, the ground-state energy $E_{gs}$ is a function of $N$; in fact, it also depends on the particle mass, on the parameters that specify $V_{\text{trap}}$ in Eq. (2.7) and $V_{\text{int}}$ in Eq. (2.8), and on Planck’s constant that appears in the Heisenberg–Born commutation relation of the components of $P$ and $R$,

$$\{a \cdot P, b \cdot R\} = \hbar a \cdot b,$$

for any two numerical vectors $a$ and $b$.

The Levy–Lieb [10, 11] constrained-search strategy finds the minimum in Eq. (2.17) in two steps. First, we choose occupation numbers $n_a$ and restrict $\rho$ by the set of constraints

$$\text{tr}(\psi(a)^\dagger \psi(a) \rho) = n_a; \quad (2.19)$$

then we consider all sets of $n_a$'s such that

$$\sum_a n_a = N. \quad (2.20)$$

Clearly, this enforces the constraint (2.14). The first step yields the energy functional

$$E[n] = \text{Min}_{\rho \rightarrow n} \{\text{tr}(H_{mp} \rho)\}, \quad (2.21)$$

where $n$, the single-particle density, stands for the list of occupation numbers and $\rho \rightarrow n$ (“$\rho$ leads to $n$”) symbolizes the constraints in Eq. (2.14); it is common practice to call $E[n]$ the density functional rather than the “energy functional of the density.” In the second step, we have

$$E_{gs}(N) = \text{Min}_{n \rightarrow N} \{E[n]\}, \quad (2.22)$$

where $n \rightarrow N$ is the constraint in Eq. (2.20). This two-step approach is useful if $E[n]$ lends itself to systematic approximations — the central challenge of DFT.

We are free to choose the modes, specified by the single-particle kets $|a\rangle$ and their adjoint bras $\langle a|$, at our convenience. The occupation numbers $n_a$, and thus the density $n$, refer to this choice and, therefore, the functional

---

2Yes, there are situations in which $\text{tr}(H\rho)$ has an infimum but no minimum; for example, when there is no trapping potential and no interaction, so that we only have kinetic energy. We are not interested in these cases and shall assume that $\text{tr}(H\rho)$ has a minimum. If you feel uncomfortable with that, just read “infimum” for each occurrence of “minimum.”
$E[n]$ depends on the choice as well. As illustrated by the three particular choices in Secs. 3, 4, 6 and the explicit Thomas–Fermi functionals in Sec. 5, the structure of $E[n]$ depends on the choice of modes very strongly. While we leave the mode dependence implicit and do not indicate it in the notation, we must remember that the density $n$ and all density functionals are context specific.

If we denote the minimizer in Eq. (2.21) by $\rho[n]$ then

$$E[n] = \text{tr}(H_{mp}\rho[n]) = \text{tr}(H_{\text{single}}\rho[n]) + \text{tr}(H_{\text{pair}}\rho[n]) = E_{\text{single}}[n] + E_{\text{pair}}[n], \quad (2.23)$$

where $E_{\text{single}}[n]$ and $E_{\text{pair}}[n]$ are defined jointly, not individually. Both functionals change when we modify $V_{\text{trap}}(r)$ in $H_{\text{single}}$ while not modifying $V_{\text{int}}(|r|)$ in $H_{\text{pair}}$, or modify $V_{\text{int}}(|r|)$ in $H_{\text{pair}}$ while not modifying $V_{\text{trap}}(r)$ in $H_{\text{single}}$. Upon introducing the reduced single-particle statistical operator

$$n^{(1)} = \sum_{a,a'} |a'\rangle \text{tr}(\psi(a')\rho[n]\psi(a)^\dagger) \langle a| \text{ with } \langle a|n^{(1)}|a\rangle = n_a \quad (2.24)$$

and the reduced two-particle statistical operator

$$n^{(2)} = \frac{1}{2} \sum_{a,a'} \sum_{b,b'} |a',b\rangle \text{tr}(\psi(b')\psi(a')\rho[n]\psi(a)^\dagger\psi(b)^\dagger) \langle a,b|, \quad (2.25)$$

which are functionals of the single-particle density $n$, we have

$$E_{\text{single}}[n] = \text{tr}(H_{1p}n^{(1)}) \quad \text{and} \quad E_{\text{pair}}[n] = \text{tr}(H_{\text{int}}n^{(2)}) \quad (2.26)$$

for the density functionals of the single-particle energy and the pair energy. There are many-particle traces in Eqs. (2.23)–(2.25), and a single-particle trace as well as a two-particle trace in Eq. (2.26).

We incorporate the constraint of Eq. (2.20) into the density functional with the aid of a Lagrange multiplier $\mu$, the chemical potential,

$$E[n,\mu] = E[n] + \mu N - \mu \sum_a n_a, \quad (2.27)$$

and then the ground-state energy is the stationary value of $E[n,\mu]$,

$$E_{\text{gs}}(N) = \text{Ext}_{n=N,\mu} \{E[n,\mu]\}. \quad (2.28)$$

When $N$ is integer, the density functional $\rho[n]$ is composed of terms with $K = L = N$ in Eq. (2.14); when $N$ is noninteger, $N_1 < N < N_2 = N_1 + 1$, $\rho[n]$ is composed of terms with $K = L = N_1$ or $K = L = N_2$; see Refs. [16–19] and references therein.
While this extremum can be a minimum, usually it is a saddle point. In any case, the ground-state values of the density and the chemical potential, \( n_{gs} \) and \( \mu_{gs} \), obey
\[
\frac{\partial}{\partial n_a} E[n] = \mu, \quad N = \sum_a n_a, \quad (2.29)
\]
so that
\[
E_{gs}(N) = E[n_{gs}]. \quad (2.30)
\]

3. Configuration-space functionals
In traditional DFT with its extensive literature \([1,2]\) the emphasis is on the three-dimensional configuration space. This corresponds to
\[
\psi(a) \rightarrow \psi_\sigma(r), \quad (3.1)
\]
which annihilates a particle with spin label \( \sigma \) at position \( r \). The symbolic summation over the mode label \( a \) is realized by summation over \( \sigma \) and integration over \( r \), as exemplified by the number operator
\[
N = \sum_\sigma \int (dr) \psi_\sigma(r)\psi_\sigma(r)^\dagger, \quad (3.2)
\]
where \( \sigma \) has two values for the spin-\( \frac{1}{2} \) fermions under consideration and \((dr)\) is the spatial volume element. The third line in Eq. (2.6) now reads
\[
\psi_\sigma(r)\psi_\sigma'(r')^\dagger + \psi_\sigma'(r')\psi_\sigma(r) = \delta_{\sigma,\sigma'}\delta(r - r'), \quad (3.3)
\]
as anticipated in footnote\(^1\).

With \( H_{1p} \) in Eq. (2.7) and \( H_{int} \) in Eq. (2.8), we have
\[
\langle a|H_{1p}|a'\rangle \rightarrow \langle r, \sigma|\left(\frac{1}{2m}p^2 + V_{\text{trap}}(R)\right)|r', \sigma'\rangle = \delta_{\sigma,\sigma'}\delta(r - r'), \quad (3.4)
\]
and
\[
\langle a, b|H_{\text{int}}|a', b'\rangle \rightarrow \langle r_1, \sigma_1; r_2, \sigma_2|V_{\text{int}}(|R_1 - R_2|)|r'_1, \sigma'_1; r'_2, \sigma'_2\rangle = \delta_{\sigma_1, \sigma'_1}\delta_{\sigma_2, \sigma'_2}\delta(r_1 - r'_1)\delta(r_2 - r'_2)V_{\text{int}}(|r_1 - r_2|), \quad (3.5)
\]
\(^1\)While there are one- and two-dimensional variants, also for the momentum-space functionals of Sec. 3 we elaborate on the three-dimensional case only.
which yield

\[ H_{\text{single}} = \sum_{\sigma} \int (d\mathbf{r}) \psi_{\sigma}(\mathbf{r})^\dagger \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{trap}}(\mathbf{r}) \right) \psi_{\sigma}(\mathbf{r}) \]  

(3.6)

and

\[ H_{\text{pair}} = \frac{1}{2} \sum_{\sigma,\sigma'} \int (d\mathbf{r})(d\mathbf{r}') \psi_{\sigma}(\mathbf{r})^\dagger \psi_{\sigma'}(\mathbf{r}')^\dagger V_{\text{int}}(|\mathbf{r} - \mathbf{r}'|) \psi_{\sigma'}(\mathbf{r}') \psi_{\sigma}(\mathbf{r}) . \]  

(3.7)

The analog of Eq. (2.19) is the spatial single-particle density

\[ n(\mathbf{r}) = \text{tr} \left( \sum_{\sigma} \psi_{\sigma}(\mathbf{r})^\dagger \psi_{\sigma}(\mathbf{r}) \rho \right) , \]  

(3.8)

where the two spin components are added. It is also possible — and, strictly speaking, more in line with Eq. (2.19) — to use both spin components

\[ n_{\sigma}(\mathbf{r}) = \text{tr} \left( \psi_{\sigma}(\mathbf{r})^\dagger \psi_{\sigma}(\mathbf{r}) \rho \right) \]  

(3.9)

and deal with the corresponding “spin-density functionals;” see Ref. [20] and the references therein. We consider only the usual spin-summed density of Eq. (3.8) and note that

\[ E_{\text{single}} = E_{\text{kin}} + \int (d\mathbf{r}) V_{\text{trap}}(\mathbf{r}) n(\mathbf{r}) \]  

(3.10)

has an exactly known functional for the potential energy of the trapping forces plus a functional for the kinetic energy that is jointly defined with the pair-energy functional,

\[ E_{\text{kin}} + E_{\text{pair}} = \text{Min}_{\rho \rightarrow n} \left\{ \text{tr} \left( (H_{\text{kin}} + H_{\text{pair}}) \rho \right) \right\} , \]  

(3.11)

where

\[ H_{\text{kin}} = \sum_{\sigma} \int (d\mathbf{r}) \psi_{\sigma}(\mathbf{r})^\dagger \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \psi_{\sigma}(\mathbf{r}) \]  

(3.12)

is the kinetic-energy contribution to \( H_{\text{single}} \) in Eq. (3.6). Both \( E_{\text{kin}} \) and \( E_{\text{pair}} \) change when we modify \( V_{\text{int}}(|\mathbf{r}|) \) in \( H_{\text{pair}} \).

We incorporate the analog of Eq. (2.20) into the functional and have

\[ E[n,\mu] = E[n] + \mu N - \mu \int (d\mathbf{r}) n(\mathbf{r}) \]

\[ = E_{\text{kin}} + \int (d\mathbf{r}) V_{\text{trap}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{pair}} + \mu N - \mu \int (d\mathbf{r}) n(\mathbf{r}) , \]  

(3.13)
whose stationary value is the ground-state energy in accordance with Eq. (2.28). The partial derivative \( \frac{\partial}{\partial n_a} \) is the functional derivative \( \frac{\delta}{\delta n(r)} \) now, so that \( n_{gs}(r) \) and \( \mu_{gs} \) solve

\[
\delta n(r) : \quad \mu - \frac{\delta}{\delta n(r)} E_{\text{kin}}[n] = V_{\text{trap}}(r) + \frac{\delta}{\delta n(r)} E_{\text{pair}}[n],
\]

and \( E_{gs} = E[n_{gs}] \) follows.

The Hohenberg–Kohn theorem [21] states that different trapping forces lead to different ground-state densities and, in this sense, the \( V_{\text{trap}}(r) \) in Eq. (3.6) is a functional of \( n_{gs} \), and then \( \rho_{gs} \) can be regarded as a functional of \( n_{gs} \). This aspect of DFT, despite its great historical importance, is not central to the Levy–Lieb constrained-search approach that we are following. In particular, the functional \( E[n, \mu] \) is well-defined also for densities \( n(r) \) that do not arise as the ground-state densities of a Hamilton operator \( H_{\text{mp}} = H_{\text{single}} + H_{\text{pair}} \) with the ingredients of Eqs. (3.6) and (3.7).

Mindful of the lessons of the Hartree–Fock method of approximate many-particle wave functions [22, 23] and the Kohn–Sham scheme in DFT [24], we regard the right-hand side in Eq. (3.14a) as an effective single-particle potential energy \( V(r) \),

\[
\frac{\delta}{\delta n(r)} E_{\text{kin}}[n] = \mu - V(r) .
\]

The Legendre transformation

\[
E_{\text{kin}}[n] \to E_{\text{kin}}[n] - \int (dr) (\mu - V(r)) n(r) = E_{1}[V - \mu]
\]

introduces the single-particle functional

\[
E_{1}[V - \mu] = \text{tr} \left( \left( H_{\text{kin}} + \sum_{\sigma} \int (dr) \psi_{\sigma}(r)^\dagger (V(r) - \mu) \psi_{\sigma}(r) \right) \rho[n] \right) .
\]

We switch from \( E_{\text{kin}}[n] \) in the density functional \( E[n, \mu] \) to \( E_{1}[V - \mu] \) in the density potential functional

\[
E[n, V, \mu] = E_{1}[V - \mu] - \int (dr) (V(r) - V_{\text{trap}}(r)) n(r) + E_{\text{pair}}[n] + \mu N ,
\]

where \( n(r), V(r), \) and \( \mu \) are independent variables; see also Ref. [25]. The ground-state energy

\[
E_{gs}(N) = \text{Ext}_{n \to N, V, \mu} \{ E[n, V, \mu] \} = E[n_{gs}, V_{gs}, \mu_{gs}]
\]
is known once \( n_{gs}, V_{gs}, \) and \( \mu_{gs} \) are found as the self-consistent solution of

\[
\delta n(r) : \quad V(r) = V_{\text{trap}}(r) + \frac{\delta}{\delta n(r)} E_{\text{pair}}[n], \quad (3.20a)
\]

\[
\delta V(r) : \quad n(r) = \frac{\delta}{\delta V(r)} E_1[V - \mu], \quad (3.20b)
\]

\[
\delta \mu : \quad N = -\frac{\partial}{\partial \mu} E_1[V - \mu]. \quad (3.20c)
\]

Equation (3.20a) ensures that the effective potential energy equals the right-hand side of Eq. (3.14a), and Eqs. (3.20b) and (3.20c) together enforce the correct integral of the density \( n(r) \), the constraint in Eq. (3.14b).

We convert \( E[n, V, \mu] \) into \( E[n, \mu] \) by enforcing Eq. (3.20b), and get a new functional \( E[V, \mu] \) upon eliminating \( n(r) \) by enforcing Eq. (3.20a). It is, however, often not possible to perform the conversions to \( E[n, \mu] \) or \( E[V, \mu] \) for an actual, approximate, explicit functional \( E[n, V, \mu] \).

The main advantage of \( E_1[V - \mu] \) over \( E_{\text{kin}}[n] \) is that it is easier to approximate \( E_1[V - \mu] \) than \( E_{\text{kin}}[n] \). We note first that

\[
E_1[V - \mu] = \sum_{\sigma, \sigma'} \int (dr)(dr') \langle r, \sigma | \left( \frac{1}{2m} P^2 + V(R) - \mu \right) | r', \sigma' \rangle
\]

\[
\times \text{tr} \left( \psi_{\sigma'}(r') \rho[n] \psi_{\sigma}(r)^\dagger \right)
\]

\[
= \text{tr} \left( (H - \mu)n^{(1)} \right), \quad (3.21)
\]

where

\[
H = \frac{1}{2m} P^2 + V(R) \quad (3.22)
\]

is the effective single-particle Hamilton operator and \( n^{(1)} \) is the reduced single-particle statistical operator

\[
n^{(1)} = \sum_{\sigma, \sigma'} \int (dr)(dr') | r', \sigma' \rangle \text{tr} \left( \psi_{\sigma'}(r') \rho[n] \psi_{\sigma}(r)^\dagger \right) \langle r, \sigma | , \quad (3.23)
\]

the version of Eq. (2.24) that applies in the present context. The traces in Eq. (3.23) and the second line in Eq. (3.21) are many-particle traces, whereas the trace in the final line in Eq. (3.21) is a single-particle trace.

It follows that \( E_1[V - \mu] \) is an expectation value of \( H - \mu \), a weighted sum of the eigenvalues of \( H - \mu \), and therefore it is the trace of an operator-valued function of \( H - \mu \),

\[
E_1[V - \mu] = \text{tr} \left( \mathcal{E}(H - \mu) \right). \quad (3.24)
\]
The implicit dependence of $E_{\text{kin}}[n]$, and as a consequence also of $E_1[V - \mu]$, on $V_{\text{int}}(|r|)$ — recall the remark after Eq. (3.12) — prevents us from stating the actual $\mathcal{E}(H - \mu)$. For a system of noninteracting fermions, Pauli’s exclusion principle implies that

$$\mathcal{E}(H - \mu) = (H - \mu)\eta(\mu - H) \quad \text{when } V_{\text{int}}(|r|) = 0,$$

(3.25)

where all single-particle states with $H < \mu$ are occupied, those with $H > \mu$ are unoccupied, and those with $H = \mu$ are partially occupied as required by Eq. (3.20c). 

$$N = -\frac{\partial}{\partial \mu} \text{tr}(\mathcal{E}(H - \mu)) = \text{tr}(\eta(\mu - H));$$

(3.26)

$\eta(x)$ denotes Heaviside’s unit step function with any value between 0 and 1 for $x = 0$. Partial occupation for $H = \mu$ occurs when $N$ is noninteger; it can also happen for integer $N$ if $\mu$ is a degenerate eigenvalue of $H$.

In the Kohn–Sham scheme, we proceed from

$$E[n] = E_{\text{kin}}^{(0)}[n] + \int (dr) V_{\text{trap}}(r)n(r) + E_{\text{pair}}^{(c)}[n]$$

(3.27)

with the density functional

$$E_{\text{kin}}^{(0)}[n] = \text{Min}_{\rho \rightarrow n} \{ \text{tr}(H_{\text{kin}}\rho) \}$$

(3.28)

for the kinetic energy of noninteracting fermions and

$$E_{\text{pair}}^{(c)}[n] = E_{\text{pair}}[n] + E_{\text{kin}}[n] - E_{\text{kin}}^{(0)}[n],$$

(3.29)

which is an amended pair-energy functional that includes the difference between $E_{\text{kin}}[n]$ and $E_{\text{kin}}^{(0)}[n]$. If we then use $E_{\text{kin}}^{(0)}[n]$ in Eqs. (3.15) and (3.16) instead of $E_{\text{kin}}[n]$, we arrive at

$$E^{(0)}[n, V, \mu] = E_{\text{kin}}^{(0)}[V - \mu] - \int (dr) (V(r) - V_{\text{trap}}(r))n(r)$$

$$+ E_{\text{pair}}^{(c)}[n] + \mu N,$$

(3.30)

with

$$E_{\text{kin}}^{(0)}[V - \mu] = \text{tr}\{(H - \mu)\eta(\mu - H)\}.$$ 

(3.31)

While we now have an explicit expression for $E_{\text{kin}}^{(0)}[V - \mu]$ and are no longer facing the challenge of determining $\mathcal{E}(H - \mu)$, we have the new task of finding a good approximation for $E_{\text{kin}}[n] - E_{\text{kin}}^{(0)}[n]$ in addition to the need of approximating $E_{\text{pair}}[n]$. It is common to write

$$E_{\text{pair}}^{(c)}[n] = \frac{1}{2} \int (dr)(dr') n(r)V_{\text{int}}(|r - r'|)n(r') + E_{\text{xc}}[n],$$

(3.32)
the sum of the *Hartree energy* and the *exchange-correlation* functional $E_{xc}[n]$. Many approximations for $E_{xc}[n]$ have been proposed, some much more popular than others; we shall not dive into this ocean and refer the reader to the discussion in Ref. [2].

The defining feature of the Kohn–Sham scheme is the evaluation of the traces in Eqs. (3.31), (3.26), and

\[
n(r) = \frac{\delta}{\delta V(r)} E_{1}^{(0)}[V - \mu] = \text{tr}(\delta(R - r)\eta(\mu - H)) = \sum_{\sigma} \langle r, \sigma | \eta(\mu - H) | r, \sigma \rangle
\]

(3.33)

in terms of the single-particle eigenstates (“orbitals”) and eigenvalues of $H$. In marked contrast, orbital-free DFT aims at approximate expressions for $E_{1}[V - \mu]$ or $E_{1}^{(0)}[V - \mu]$ in conjunction with corresponding approximations for $E_{\text{pair}}[n]$ or $E_{\text{pair}}^{(c)}[n]$ in terms of their variables. Both approaches have their merits.

4. Momentum-space functionals

One version of nontraditional DFT that has been developed to some extent [4–9] deals with functionals of the momentum-space density $n(p)$, where we have

\[
\psi(a) \rightarrow \psi_\sigma(p),
\]

(4.1)

which annihilates a spin-$\frac{1}{2}$ fermion with spin label $\sigma$ and momentum $p$. Then

\[
\psi_\sigma(p)\psi_{\sigma'}(p')^\dagger + \psi_{\sigma'}(p')^\dagger \psi_\sigma(p) = \delta_{\sigma,\sigma'}\delta(p - p'),\tag{4.2a}
\]

\[
N = \sum_{\sigma} \int (dp) \psi_\sigma(p)^\dagger \psi_\sigma(p),\tag{4.2b}
\]

\[
n(p) = \text{tr} \left( \sum_{\sigma} \psi_\sigma(p)^\dagger \psi_\sigma(p) \rho \right),\tag{4.2c}
\]

are the analogs of Eqs. (3.3), (3.2), and (3.8), respectively. With the Fourier transformed potential energy functions

\[
U_{\text{trap}}(p) = \int \frac{(dr)}{(2\pi \hbar)^3} e^{-i p \cdot r / \hbar} V_{\text{trap}}(r)
\]

(4.3)

and

\[
U_{\text{int}}(|p|) = \int \frac{(dr)}{(2\pi \hbar)^3} e^{-i p \cdot r / \hbar} V_{\text{int}}(|r|),\tag{4.4}
\]
the momentum-space versions of Eqs. (3.6) and (3.7) read

\[
H_{\text{single}} = \sum_{\sigma} \int (dp) \psi_{\sigma}(p)^\dagger \left( \frac{1}{2m} p^2 \psi_{\sigma}(p) \right) \nonumber \\
+ \sum_{\sigma} \int (dp)(dp') \psi_{\sigma}(p)^\dagger U_{\text{trap}}(p - p') \psi_{\sigma}(p') \nonumber \\
= H_{\text{kin}} + H_{\text{trap}} \quad (4.5)
\]

and

\[
H_{\text{pair}} = \frac{1}{2} \sum_{\sigma,\sigma'} \int (dp)(dp') \psi_{\sigma}(p)^\dagger \psi_{\sigma'}(p')^\dagger U_{\text{int}}(|p - p'|) \psi_{\sigma'}(p') \psi_{\sigma}(p). \quad (4.6)
\]

The energy functional of the momentum-space density,

\[
E[n] = \int (dp) \left( \frac{1}{2m} p^2 n(p) + E_{\text{trap}}[n] + E_{\text{pair}}[n] \right), \quad (4.7)
\]

has an exactly known functional for the kinetic energy and functionals for the potential energy of the trapping forces and the pair energy that are jointly defined by

\[
E_{\text{trap}}[n] + E_{\text{pair}}[n] = \min_{\rho \rightarrow n} \left\{ \text{tr} \left( (H_{\text{trap}} + H_{\text{pair}}) \rho \right) \right\} \\
= \text{tr}(H_{\text{trap}}\rho[n]) + \text{tr}(H_{\text{pair}}\rho[n]), \quad (4.8)
\]

where \( \rho \rightarrow n \) stands for the constraint in Eq. (4.2c). Both \( E_{\text{trap}}[n] \) and \( E_{\text{pair}}[n] \) change when we modify \( V_{\text{trap}}(r) \) or \( V_{\text{int}}(|r|) \).

The momentum-space analog of Eq. (3.15) is

\[
\frac{\delta}{\delta n(p)} E_{\text{trap}}[n] = \mu - T(p), \quad (4.9)
\]

which introduces the effective kinetic energy \( T(p) \); the analogs of Eqs. (3.16) and (3.17) are

\[
E_1[T - \mu] = E_{\text{trap}}[n] - \int (dp) \left( \mu - T(p) \right)n(p) \nonumber \\
= \text{tr} \left( \left( H_{\text{trap}} + \sum_{\sigma} \int (dp) \psi_{\sigma}(p)^\dagger (T(p) - \mu) \psi_{\sigma}(p) \right) \rho[n] \right), \quad (4.10)
\]

Note that the momentum-space formalism is universal in the dispersal relation: We may substitute the quadratic dispersion \( p^2/(2m) \) with, for example, one proportional to \( |p| \), with no change in \( E_{\text{trap}}[n] \) and \( E_{\text{pair}}[n] \).
which takes us to the analog of Eq. (3.18),

$$E[n, T, \mu] = E_1[T - \mu] - \int (d\mathbf{p}) \left( T(\mathbf{p}) - \frac{1}{2m} \mathbf{p}^2 \right) n(\mathbf{p})$$

$$+ E_{\text{pair}}[n] + \mu N,$$

(4.11)

The ground-state values $n_{gs}, T_{gs}, \mu_{gs}$ are the self-consistent solution of

$$\delta n(\mathbf{p}) : \quad T(\mathbf{p}) = \frac{1}{2m} \mathbf{p}^2 + \frac{\delta}{\delta n(\mathbf{p})} E_{\text{pair}}[n],$$

$$\delta T(\mathbf{p}) : \quad n(\mathbf{p}) = \frac{\delta}{\delta T(\mathbf{p})} E_1[T - \mu],$$

$$\delta \mu : \quad N = - \frac{\partial}{\partial \mu} E_1[T - \mu],$$

(4.12)

which are the momentum-space analogs of Eqs. (3.20).

Further, the analog of Eq. (3.24) reads

$$E_1[T - \mu] = \text{tr} (\mathcal{E}(H - \mu))$$

(4.13)

with

$$H = T(\mathbf{P}) + V_{\text{trap}}(\mathbf{R}),$$

(4.14)

and Eq. (3.25) continues to apply for noninteracting fermions. The momentum-space Kohn–Sham scheme is fully analogous to that of Eqs. (3.27)–(3.33) in configuration space; details can be found in Ref. [8].

We note that the single-particle Hamilton operators in Eqs. (3.22) and (4.14) do not commute and, therefore, have different sets of Kohn–Sham orbitals. It follows that the Kohn–Sham orbitals cannot be Löwdin’s “natural orbitals” [26], the eigenstates of $n^{(1)}$ for $\rho[n] = \rho[n_{gs}]$ in Eq. (3.23).

5. Thomas–Fermi atoms in configuration and momentum space

When the spin-$\frac{1}{2}$ fermions are electrons in an atom with nuclear charge $Ze$, we have a Coulomb potential for both $V_{\text{trap}}(\mathbf{r})$ and $V_{\text{int}}(|\mathbf{r}|),$  

$$V_{\text{trap}}(\mathbf{r}) = -\frac{Ze^2}{|\mathbf{r}|}, \quad V_{\text{int}}(|\mathbf{r}|) = \frac{e^2}{|\mathbf{r}|},$$

(5.1)

for which

$$U_{\text{trap}}(\mathbf{p}) = -\frac{Ze^2}{2\pi^2\hbar} \frac{1}{p^2}, \quad U_{\text{int}}(|\mathbf{p}|) = \frac{e^2}{2\pi^2\hbar} \frac{1}{p^2}$$

(5.2)

are the respective Fourier transforms. In the Thomas–Fermi model [27, 28] for atoms we use the leading semiclassical approximations for $E_1[V - \mu]$
and $E_1[T-\mu]$, with $\mu < 0$ here, and approximate $E_{\text{pair}}[n]$ by the dominant Hartree energy. The latter is

$$E_{\text{pair}}^{(\text{TF})}[n] = \frac{1}{2} \int \frac{(d\mathbf{r})(d\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) e^{2|\mathbf{r} - \mathbf{r}'|/|\mathbf{r}|} n(\mathbf{r}')$$

(5.3)

in configuration space and

$$E_{\text{pair}}^{(\text{TF})}[n] = \frac{1}{2} \int \frac{(d\mathbf{p})(d\mathbf{p}')}{(2\pi\hbar)^3} (3\pi^2)^{1/3} \frac{e^2}{2\pi^2\hbar} \left( \frac{n^{2/3} - \frac{1}{5} n^{5/3}}{n^2} \right)$$

(5.4)

with $n > = \text{Max}\{n(p), n(p')\}$ and $n_\prec = \text{Min}\{n(p), n(p')\}$ in momentum space.

The semiclassical approximation of the single-particle functionals replaces the quantum mechanical traces in Eqs. (3.24) and (4.13) by classical phase space integrals after approximating $E_1[V-\mu]$ and $E_1[T-\mu]$ by the respective Kohn–Sham expressions. Accordingly, we have

$$E_1^{(\text{TF})}[V-\mu] = 2 \int \frac{(d\mathbf{r})(d\mathbf{p})}{(2\pi\hbar)^3} \left( \frac{p^2}{2m} + V(r) - \mu \right) \eta \left( \mu - \frac{p^2}{2m} - V(r) \right)$$

(5.5)

in configuration space and

$$E_1^{(\text{TF})}[T-\mu] = 2 \int \frac{(d\mathbf{r})(d\mathbf{p})}{(2\pi\hbar)^3} \left( T(p) - \frac{Ze^2}{|r|} - \mu \right) \eta \left( \mu - T(p) + \frac{Ze^2}{|r|} \right)$$

(5.6)

in momentum space, where the factor of two is the spin multiplicity. Upon evaluating the $\mathbf{p}$ integral in Eq. (5.5) and the $\mathbf{r}$ integral in Eq. (5.6), we arrive at the respective Thomas–Fermi functionals,

$$E^{(\text{TF})}[n, V, \mu] = - \int (d\mathbf{r}) \frac{1}{15\pi^2\hbar^3 m} \left[ 2m(\mu - V(r)) \right] +$$

$$- \int (d\mathbf{r}) \left( V(r) + \frac{Ze^2}{|r|} \right) n(r) +$$

$$\frac{1}{2} \int (d\mathbf{r})(d\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(r') + \mu N$$

(5.7)

with $[x]_+ = x\eta(x)$ and

$$E^{(\text{TF})}[n, T, \mu] = - \int (d\mathbf{p}) \frac{1}{6\pi^2} \left( \frac{Ze^2/\hbar}{T(p) - \mu} \right)^2$$

$$- \int (d\mathbf{p}) \left( T(p) - \frac{p^2}{2m} \right) n(p) +$$

$$\frac{1}{2} \int (d\mathbf{p})(d\mathbf{p}') \left( \frac{3}{2\pi} \right)^{2/3} \frac{e^2}{2\hbar} \left( \frac{n^{2/3} - \frac{1}{5} n^{5/3}}{n^2} \right) + \mu N.$$
Although these functionals are obviously quite different in structure, they are equivalent in their implications because the two step functions in Eqs. (5.5) and (5.6) select the same classically allowed region in phase space for the stationary values of $V(r)$, $T(p)$, and $\mu$,

$$
\eta \left( \mu_{gs} - \frac{p^2}{2m} - V_{gs}(r) \right) = \eta \left( \mu_{gs} - T_{gs}(p) + \frac{Ze^2}{|r|} \right); \quad (5.9)
$$

see Refs. [6, 9] for the details.

Once we improve on the Thomas–Fermi approximation and include the leading correction — the Scott correction [29] for the strongly bound electrons, that is — the respective Thomas–Fermi–Scott models [7,30] are not equivalent. The same remark applies at the next level of approximation where we account for the exchange energy and the leading quantum correction to the phase space integrals in Eqs. (5.5) and (5.6).

6. Single-particle-exact functionals

The configuration-space functional $E_{\text{single}}[n]$ in Eq. (3.10) treats the potential energy of the trapping forces exactly and, in all practical applications, requires a good approximation for the kinetic-energy contribution $E_{\text{kin}}[n]$. The momentum-space functional in Eq. (4.7) is exact for the kinetic energy but needs an approximation for $E_{\text{trap}}[n]$. It is also possible to have an exact density functional for both terms in $E_{\text{single}}[n] = E_{\text{kin}}[n] + E_{\text{trap}}[n]$, not just for one or the other.

For this purpose, we choose modes that refer to the eigenstates of $H_{\text{single}}$, so that

$$
|a\rangle \rightarrow |k,\sigma\rangle, \quad \psi(a) \rightarrow \psi_{k,\sigma}, \quad (6.1)
$$

where

$$
H_{1p}(R, P)|k,\sigma\rangle = |k,\sigma\rangle \varepsilon_k \quad \text{for} \quad k = 0, 1, 2, \ldots \quad (6.2)
$$

with $\varepsilon_k \geq \varepsilon_{k'}$ when $k > k'$ for the spin-degenerate eigenvalues. Then, the occupation numbers

$$
n_k = \sum_\sigma \text{tr} \left( \psi_{k,\sigma}^\dagger \psi_{k,\sigma} \rho \right) \quad (6.3)
$$

are restricted by $0 \leq n_k \leq 2$ for all $k$.\footnote{There could be scattering states with continuous eigenvalues in addition to the discrete bound states of $H_{1p}$ that we are considering. The completeness relation in Eq. (2.3) needs the scattering states as well as the bound states. Following the practice of Kohn–Sham calculations, we regard the scattering states as unoccupied.} The energy functional of Eq. (2.22)
is

\[ E[n] = \sum_{k=0}^{\infty} \varepsilon_k n_k + E_{\text{pair}}[n] \]  

(6.4)

with

\[ E_{\text{pair}}[n] = \min_{\rho \rightarrow n} \{ \text{tr}(H_{\text{pair}} \rho) \} = \text{tr}(H_{\text{pair}} \rho[n]) \],

(6.5)

where \( \rho \sim n \) enforces the constraint of Eq. (6.3). Indeed, we have an exact density functional for \( E_{\text{single}}[n] \) and, as always, need to approximate \( E_{\text{pair}}[n] \).

Very much of this territory is unexplored. Work on approximate pair-energy functionals is ongoing and progressing [31,32]. We have, for example, an algorithm for generating a full single-particle density matrix from the prechosen diagonal elements, the occupation numbers in Eq. (6.3), as well as a Thomas–Fermi-type approximation for the off-diagonal matrix elements. With that at hand, we follow Dirac’s guidance [33] and arrive at a two-particle density matrix in Hartree–Fock approximation, which in turn yields a value for the trace in Eq. (6.5). Alternatively, when the pair interaction is weak, we can approximate \( E_{\text{pair}}[n] \) in second-order perturbation theory [34].

Appendix: Semiclassical eigenvalues

Semiclassical approximations — and their unreasonable accuracy — are central to DFT as emphasized by Okun and Burke in Ref. [2]. The phase space integrals in Eqs. (5.5) and (5.6) are to the point.

Approximate eigenvalues of Hamilton operators, obtained by the WKB method [35–37], play an important role, too. For one-dimensional Hamilton operators of the standard form

\[ H(X, P) = \frac{1}{2m} P^2 + V(X) \]  

(A.1)

we find an approximation for the \( k \)th eigenvalue by the well-known quantization rule

\[ k + \frac{1}{2} = \int \frac{dx \ dp}{2\pi \hbar} \eta(E_k - H(x, p)) \]

\[ = \frac{1}{\pi \hbar} \int dx \left[ 2m(E_k - V(x)) \right]^{1/2} \]  

(A.2)

with \( k = 0, 1, 2, \ldots \). The corresponding expression for an eigenvalue of the isotropic three-dimensional Hamilton operator

\[ H(R, P) = \frac{1}{2m} P^2 + V(|R|) \]  

(A.3)
is equally familiar,

$$k + \frac{1}{2} = \frac{1}{\pi \hbar} \int dr \left[ 2m \left( E_{k,l} - \frac{\hbar^2}{2m} \frac{(l + \frac{1}{2})^2}{r^2} - V(r) \right) \right]^{1/2}, \quad (A.4)$$

where \( k = 0, 1, 2, \ldots \) is the radial quantum number and \( l = 0, 1, 2, \ldots \) is the angular momentum quantum number, as the sector with \( L^2 = (R \times P)^2 = l(l+1)\hbar^2 \) is considered. The replacement \( l(l+1) \rightarrow (l + \frac{1}{2})^2 \) is the so-called Langer correction \[38\]. It is remarkable that Eq. (A.4) yields the exact Bohr energies for the Coulomb potential \( V(r) = -Ze^2/r \), rather than having systematically small errors in the correspondence limit of large quantum numbers. The performance of Eq. (A.4) is better than one should reasonably expect.

Let us put spin multiplicity aside and consider

$$\nu(\varepsilon) = \text{tr} \left( \eta(\varepsilon - H(R, P)) \right), \quad (A.5)$$

which is the count of eigenvalues of \( H(R, P) \) below the threshold \( \varepsilon \). The value of \( \nu(\varepsilon) \) is an integer when \( \varepsilon \) is between successive eigenvalues and equals any intermediate noninteger when \( \varepsilon \) is an eigenvalue of \( H(R, P) \); the graph of \( \nu(\varepsilon) \) is a stair case. The evaluation of the trace by a phase space integral,

$$\nu(\varepsilon) = \int \frac{(dr)(dp)}{(2\pi\hbar)^3} \left[ \eta(\varepsilon - H(R, P)) \right]_w(r, p), \quad (A.6)$$

involves the Wigner function \[39\] \[40\], sometimes called Weyl symbol, of the operator \( \eta(\varepsilon - H) \). For an operator-valued function of \( H \) we have the semiclassical approximation

$$[f(H)]_w(r, p) \approx f(H_w(r, p)), \quad (A.7)$$

where we neglect all quantum corrections — technically speaking, these are terms involving even powers of Planck’s constant times the Poisson-bracket differential operator; see, for example, the appendix in Ref. \[41\].

Quite generally, then,

$$\text{tr} \left( f(H(R, P)) \right) = \int \frac{(dr)(dp)}{(2\pi\hbar)^3} \left[ f(H(R, P)) \right]_w(r, p) \approx \int \frac{(dr)(dp)}{(2\pi\hbar)^3} f(H_w(r, p)) \quad (A.8)$$

provides a semiclassical approximation for the trace of a function of the Hamilton operator, and this can be improved by including some of the
quantum corrections. We have examples of Eq. (A.8) in Eqs. (5.5) and (5.6) since

\[ T(P) + V(R) \big|_w(r, p) = T(p) + V(r). \quad \text{(A.9)} \]

When we apply Eq. (A.7) to Eq. (A.6), we approximate the stair-case function by a very smooth function of \( \varepsilon \), which suggests to determine approximate eigenvalues of \( H \) by

\[ k + \frac{1}{2} = \int \frac{(dr)(dp)}{(2\pi\hbar)^3} \eta(E_k - H_w(r, p)). \quad \text{(A.10)} \]

This works best for the one-dimensional Hamilton operators of Eq. (A.1) for which Eq. (A.10) becomes Eq. (A.2).

The application to an angular-momentum sector of an isotropic three-dimensional Hamilton operator as in Eq. (A.3) requires a proper reduction to an effective one-dimensional Hamilton operator for the radial motion. With

\[ R = |R|, \quad \Gamma = \frac{1}{2}(R \cdot P + P \cdot R), \quad [R, \Gamma] = i\hbar R \quad \text{(A.11)} \]

we have

\[ P^2 = \frac{1}{R} \left( \Gamma^2 + L^2 + \frac{1}{4} \hbar^2 \right) \frac{1}{R} \rightarrow \frac{1}{R} \left( \Gamma^2 + (l + \frac{1}{2})^2 \hbar^2 \right) \frac{1}{R}, \quad \text{(A.12)} \]

where we restrict to an angular-momentum sector in the last step, and recognize the origin of the Langer correction. For the Hamilton operator in Eq. (A.3) this means

\[ H(R, P) \rightarrow H_l(R, \Gamma) = \frac{1}{2m} \frac{1}{R} \left( \Gamma^2 + (l + \frac{1}{2})^2 \hbar^2 \right) \frac{1}{R} + V(R). \quad \text{(A.13)} \]

We introduce a proper Heisenberg \( X, P \) pair in accordance with

\[ \kappa R = e^{\kappa X}, \quad \kappa \Gamma = P, \quad [X, P] = i\hbar, \quad \text{(A.14)} \]

where \( \kappa \) is a reference wave number, a reciprocal length, that ensures the correct metrical dimensions, and obtain

\[ H_l^{(1D)}(X, P) = e^{-\kappa X} \frac{P^2}{2m} e^{-\kappa X} + \frac{(\hbar \kappa)^2}{2m} (l + \frac{1}{2})^2 e^{-2\kappa X} + V \left( \kappa^{-1} e^{\kappa X} \right). \quad \text{(A.15)} \]

The replacements \( X \rightarrow x, \ P \rightarrow p \) turn this \( H_l^{(1D)}(X, P) \) into its Wigner function, so that

\[ k + \frac{1}{2} = \int \frac{dx \ dp}{2\pi\hbar} \eta \left( E_{k,l} - H_l^{(1D)}(x, p) \right) \quad \text{(A.16)} \]
is the proper analog of Eq. (A.10). After evaluating the \( p \) integral and switching from \( x \) to \( r = \kappa^{-1} e^{\kappa x} \), we arrive at Eq. (A.4).

This procedure does not treat \( R \) and \( P \) on equal footing. Rather than giving a privileged role to the position operator in Eq. (A.11), we can just as well single out the momentum operator and work with the pair \( P = |P| \) and \( \Gamma \). For \( V(r) = -Z e^2/r \) this “semiclassical quantization in momentum space” does not yield the exact Bohr energies. Instead, we get very good approximate eigenvalues with systematically smaller errors for larger quantum numbers; see Ref. [42] for the details.

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