Dual Characterization of the Ornstein-Zernike Equation in Moment Space

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Abstract The molecular density functional theory of fluids provides an exact theory for computing solvation free energies in implicit solvents. One of the reasons it has not received nearly as much attention as quantum density functional theory for implicit electron densities is the paucity of basis set expansions for this theory. This work constructs a minimal Hilbert space version of the Ornstein-Zernike theory over the complete spatial, rotational, and internal conformational space that leaves the choice of basis open. The basis is minimal in the sense that it is isomorphic to a choice of molecular property space (i.e. moments of the distribution), and does not require auxiliary grids. This can be exploited, since there are usually only a few ‘important’ properties for determining the structure and energetics of a molecular fluid. Two novel basis expansions are provided which emphasize either the multipolar expansion (most useful for flexible molecules) or the rotational distribution (most useful for rigid bodies described using quaternions). The perspective of this work also shows that radial truncation of the Bessel series over translation space determines an analytical extrapolation of these functions to the origin in reciprocal space.

Keywords Molecular Ornstein-Zernike · Potential distribution · Molecular density functional · Functional equations · Orlicz spaces · Computational methods · Correlation functions

1 Introduction

In this work, we show that a full expansion in terms of local, molecular fields is ‘dual’ to a basis expansion of the density function. The duality between these two approaches is exactly that between a distribution and its moments, and is a special case of the moment problem in classical probability theory.\[15\] Hence, the rotational invariant expansion of Blum\[8\] is only a particular choice which is best used to describe multipole moments of a rigid molecule. We provide two examples of moment spaces which use this transformation to eliminate rotational density space in favor of observable molecular properties.

The connection to moments of the density distribution was was implicit in the original spherical harmonic expansion of Blum\[8\] but seems to have been first used effectively by Sluckin.\[38\] Nevertheless, the
spherical invariant expansion has been the framework adopted by most later works. Interestingly, many of those later works find convenient expressions in matrix form.\cite{7} When using general potentials, Fries and coworkers noted there were difficulties associated with carrying out six-dimensional angular integrals (over rigid-body rotational degrees of freedom).\cite{21} More recent works have shown the usefulness of expressing the translational part of the Ornstein-Zernike (OZ) equation in a Cartesian grid basis.\cite{22,27,23}

Recent work by Borgis and collaborators\cite{34} has shown the usefulness of coarsening the rotational distribution into a spatial dipolar polarization density. Those works outline a path between the spherical invariant and spatial number and dipolar density representations that makes it possible to phrase solvation thermodynamics entirely in terms of latter, at least for the Stockmayer fluid. Its application to liquid water has turned out to be very successful,\cite{44} motivating extension to higher orders.\cite{24}

The mathematical motivation for this re-phrasing is the relative difficulty of working with probability distributions over molecular position and conformation space, \( x = (r, q, s) \in \Omega_1 \equiv \mathbb{R}^3 \times \text{SO}(3) \times S \), where \( r \) is the center of mass location, \( q \) is a unit quaternion describing the orientation, and \( s \in S \) describes all internal coordinates. The set \( S \) is an arbitrary space of internal molecular coordinates. In applications, the space of distribution functions over \( \Omega_1 \) is usually truncated to a finite number of basis functions. Thus, it is natural to look for physically motivated transformations of those basis functions that give more insight into molecular structure.

By following this idea through, we show how existing literature on one-component fluids of spherical particles can, in most cases, be lifted to a matrix notation valid for molecules with internal and rotational degrees of freedom. This opens new ideas for analytical and numerical investigations. Important potential application areas include examining the density-dependence of dielectric effects,\cite{31,33,17} simplifying models of solvation\cite{6,30,42} including Casimir (density fluctuation) forces,\cite{11} and extending dynamic density functional theories.\cite{2}

This work is divided into sections presenting I,II) the linear transformations between traditional projections of the 1-particle density onto a basis and field equations for average molecular properties, and III,V) a formulation of OZ and classical fluid density functional theory (DFT) directly in molecular field space. Section IV presents two alternative basis expansions – multipolar moments appropriate for general molecules and a quadrature basis for distributions over quaternions appropriate for rigid bodies. A complete application is presented in Sec. VI, where we recover in a few steps the mean-spherical approximation for dipolar hard spheres and then show how it can be adapted to investigate Casimir forces in fluids of polarizable point dipoles. These simplifications are possible because both the OZ and DFT equations are replaced by matrix multiplications and inversions (and a matrix logarithm).

\section{Problem Statement}

The usual perturbation theory is most easily stated by defining functionals,

\begin{equation}
Z[\Phi] \equiv \left\langle e^{i\Phi \cdot \hat{\rho}} \right\rangle, \quad Z_N[\Phi] \equiv \left\langle e^{i\Phi \cdot \hat{\rho}} \right\rangle_{n = N},
\end{equation}

where \( \Phi(x) \) is a (real-valued) function of the coordinates, \( x \), of one molecule and \( \hat{\rho}(x) \) is the instantaneous number density of molecules at point \( x \) (a function of the microstate). For precise definitions, see Sec. 2.1. Single-brackets denote an average over the Grand-Canonical ensemble, and double-brackets indicate the inner product,

\begin{equation}
\langle \Phi, \hat{\rho} \rangle \equiv \int_{\Omega_1} dx \; \Phi(x) \hat{\rho}(x).
\end{equation}
Then, since Eq. 1 is a moment generating function for $\hat{\rho}$, the 1-particle density is its first cumulant,

$$\rho(x|\Phi) = \frac{\delta \log Z[\Phi]}{\delta \Phi(x)}.$$  

Thermodynamic integration then provides a method for calculating the density response to ‘charging’ $\Phi_\lambda$ as $\lambda$ smoothly changes $\Phi_0 = 0$ into $\Phi_1 = \Phi$,

$$\rho(x|\Phi) = \rho(x|0) + \int_0^1 d\lambda \left\langle \frac{\partial \rho(x|\Phi_\lambda)}{\partial \Phi_\lambda} \right\rangle.$$  

It is usually the case that the pair potential can be decomposed into relative translation and internal coordinate-dependent parts, $\Phi(x) \sim \sum_{i=1}^M \phi_i(r) f_i(q,s)$, where $f: SO(3) \times S \rightarrow \mathbb{R}^M$ is some vector-valued function of the molecular conformation, $\phi: \mathbb{R}^3 \rightarrow \mathbb{R}^M$ is a vector-valued potential, and $\sim$ denotes convergence with increasing expansion order, $M$. In this case, we can work out conditions where

$$\langle \Phi, \hat{\rho} \rangle = \langle 1 \Phi, \hat{\rho} \rangle = 0,$$  

which explicitly uses the field density of molecular observables, $f$,

$$\hat{F}(r) \equiv \int dq ds (q,s) \rho(r,q,s) \sim \sum_{j=1}^n \delta(r,r_j) f(q_j,s_j).$$  

The new inner product uses the obvious definition,

$$\langle \phi, \hat{F} \rangle = \int dr \phi^\dagger(r) \hat{F}(r) \sim \sum_{j=1}^n \phi^\dagger(r_j) f(q_j,s_j),$$

where $z^\dagger$ denotes the complex-conjugate transpose of $z$. Because of this equivalence, we abuse notation to write $Z[\phi] = Z[\Phi]$.

It is equally valid to write thermodynamic integration in terms of the “molecular field,” $F(r|\phi) = \delta \log Z[\phi]/\delta \phi(r)$,

$$F(r|\phi) = F(r|0) + \int_0^1 d\lambda \left\langle \frac{\partial F(r|\phi_\lambda)}{\partial \phi_\lambda} \right\rangle.$$  

Providing a useful transformation between the first and second versions of the perturbation theory giving the integrand of Eq. 8 is the motivation for this work. These relations are then used to define a density-operator algebra and to re-state the OZ and DFT theories in moment space.

### 2.1 Technicalities

We use a hybrid between statistical mechanical and measure theory notation. The grand-Canonical ensemble is defined as a probability space over microstates, $\Omega = \{ (n, \{ x_i \}) | n = 0, 1, \ldots; x_i \in \Omega_i \}$. We always use the sigma algebra for measurable subsets of $\Omega$ without mention. Most integrals with respect to its probability measure, $d\nu_{GC}$, are written using conditional average notation,

$$\langle \hat{f}|A \rangle \equiv \frac{\int_{\Omega} d\nu_{GC}(\omega) \hat{f}(\omega) \Psi_A(A(\omega))}{\int_{\Omega} d\nu_{GC}(\omega) \Psi_A(A(\omega))}.$$
for the average of a measurable function, \( \hat{f} : \Omega \rightarrow \mathbb{R} \), in the GC ensemble using a nonnegative weighting function, \( \Psi_A(A(\omega)) \), on configuration space. The function \( \Psi_A \) is inferred from the type of \( A \). If \( A \) is a subset of configuration space (in the sigma algebra generated by \( \Omega \)), then \( \Psi_A(A(\omega)) \) is the characteristic function which is one when \( \omega \in A \) and zero otherwise. If \( A \) is a 1-particle potential energy function (scaled by \(-\beta = 1/k_B T\)), then \( \Psi \) is the exponential, \( \Psi_A(A) = \exp(\langle A, \hat{\rho} \rangle) \). Of course, this assumes the denominator is bounded and nonzero. Boundedness is guaranteed for potential functions \( A \in \hat{L}^{\exp}(\nu_{GC}) \), the convex set of Orlicz-class functions with N-function \( e^{|x|} - |x| - 1 \).[35]

In most computational applications, the function spaces for pair potential energy functions and 1-particle densities are isomorphic to a finite-dimensional Hilbert space. This will be the general setting of the current work. We also leave out explicit proofs on convergence of functions in the density, moment, and potential densities are isomorphic to a finite-dimensional Hilbert space. This will be the general setting of the current work.

\[
||A||_{\exp} = \inf_{\beta > 0} \left\{ \beta^{-1} \int_{\Omega} (e^{\beta|A|} - \beta|A|) d\nu_{GC} \right\}. \tag{10}
\]

This requires identifying almost everywhere equal functions, \( A \) (i.e. two functions are equal if they differ only inside of excluded volume regions). Equation 10 is a restatement of Theorem 3.3.13 from Ref. [35], specialized by noting \( \int_{\Omega} d\nu_{GC} = 1 \). Rigorous analysis from the Orlicz perspective will be the subject of a separate work.

In this work, \( \delta(x, y) \) is not a Dirac delta distribution, but is a reproducing kernel defined for a separable Hilbert space, \( \mathcal{H}^{\text{conf}} \), of functions on the 1-molecule translation plus configuration space \( \Omega_1 \).[3] That Hilbert space must include constant functions, but can otherwise be chosen arbitrarily. With the appropriate choice, the last step in Eq. 13 can converge asymptotically to the sum of 1-molecule interaction energies. Asymptotic convergence with respect to the dimension of \( \mathcal{H}^{\text{conf}} \) is indicated with \( \sim \). For convenience, we also assume translational degrees are separable from rotation and internal degrees of freedom, so that the reproducing kernel factors as \( \delta(x, x') = \delta(r, r') \delta(q, s; q', s') \). It is a classical result that choosing a positive-definite \( \delta(r, r') \) is equivalent to choosing \( \mathcal{H}^{\text{trs}} \), and similarly for \( \delta(q, s; q', s') \).\( \sim \mathcal{H}^{\text{conf}} \).[3] Also, we define a scaled integration measure, \( dx = dr dq ds \) so that \( \int dV = V \), the system volume, and \( \int dq dq ds = 1 \) includes whatever normalization is required for \( SO(3) \times S \). If \( q = [\sin \psi \sin \chi \sin \theta, \sin \psi \sin \chi \cos \theta, \sin \psi \cos \chi, \cos \psi]^T \) is represented as a unit quaternion on the 3-sphere, \( S^3 \), then \( dq = \sin^2(\psi) d\psi d\chi d\theta / 2\pi^2 \).

The 1-molecule density in Eq. 3 is equal to

\[
\langle \hat{\rho}(x)|\Phi \rangle = \frac{\int_{\Omega} d\nu_{GC} \hat{\rho}(x) e^{\Phi, \hat{\rho} \rangle}}{\int_{\Omega} d\nu_{GC} e^{\Phi, \hat{\rho} \rangle}}, \tag{11}
\]

where

\[
\hat{\rho}(x) = \sum_{j=1}^{n} \delta(x, x_j) \tag{12}
\]

is a family of measurable functions parameterized by \( x \). Used in this way, \( \delta(x, x') \) projects the 1-molecule Grand-canonical probability distribution into \( \mathcal{H}^{\text{trs}} \otimes \mathcal{H}^{\text{conf}} \).

The 1-particle biasing potential is related to the excess chemical potential of a solute in the following way. If the potential energy change for inserting a molecule in configuration \( y \in \Omega_1 \) is the pairwise sum of 2-body interactions,

\[
\Delta \hat{E}_y(\omega) = \sum_{j=1}^{n} U_2(x_j, y), \tag{13}
\]
then it should also be expressible as an instantaneous interaction energy with a field,
\[ \langle \Phi, \hat{\rho} \rangle \sim -\beta \Delta \hat{E}_x. \] (14)
The convergence indicated by \( \sim \) is replaced with equality when \( U_2(x, y) \) – considered as a function of \( x \) – is a member of the Hilbert space. The excess chemical potential converges to the integral over solute configurations, \( x_1 \in \Omega_1 \)[5]
\[ e^{-\beta \mu^\alpha(N,V,T)} \sim \langle Z_N[\Phi_{x_1}] | n = 1 \rangle. \] (15)
The inner average is commonly referred to as \( \beta \rho^\alpha(Y; N, V, T) \equiv -\log Z_N[\Phi_y] \), the test particle insertion free energy for a solute frozen in configuration \( y \). For particle insertion in a homogeneous, isotropic solution, \( \mu^\alpha(x) = \mu^\alpha(s) \) is independent of \( r, q \) by symmetry.

The use of the hat notation for random variables is appropriate here since, for example, \( \hat{n}(\omega) = n \) is formally a function which assigns a number to each microstate \( \omega \) just as an operator in quantum mechanics represents a classical observable by a diagonal matrix indexed by \( \omega \) \( y \) as an operator in quantum mechanics indexed by \( y \). For \( \rho \), \( F \), and \( \Delta E \), we remove the hat when an ensemble average has been taken – for example in \( \Delta E = \langle \Delta \hat{E} \rangle \). For all variables other than \( \Delta E \), we use the notation \( \Delta \hat{X} \equiv \hat{X} - \bar{X} \) to denote the difference between the instantaneous and ensemble average values (using \( dv_{GC} \)) of a random variable, \( \hat{X} \).

3 Transformation Between Formalisms and Convolution Algebra

The two formalisms are of course related by the requirement that the field be the average of the distribution, \( F(r) = \int dq'ds' f(q', s') \rho(r, q', s') \). This is a direct consequence of the definition in Eq. 6. Thus, a perturbation theory for \( \rho \) can be used to find one for \( F \).

We prove in this section that the correspondence is actually one to one whenever a finite basis is used to represent the distribution over conformation space as a function in the Hilbert space, \( H^{conf} \). This finite basis then determines the property vector, \( f \), up to linear transformation. Obviously, this requires that the density basis for \( H^{conf} \) have dimension, \( M \), equal to that of \( f \). The key relation is given by,
\[ \iint dqds \Phi(x) \delta(x, x') = \delta(r, r') \sum_{i=1}^{M} \hat{\phi}_i(r) f_i(q', s'). \] (16)
The overbar denotes complex conjugation, although we almost always work with real \( \phi, f \). Note that Eq. 16 implies Eq. 5, which proves both operators, \( \Delta \hat{E} \), and the corresponding free energy functionals, \( Z \), are equivalent.

To prove our assertion above, we must show the validity of Eq. 16 and that the translation from \( \rho \) to \( F \) (Eq. 6) can be inverted to find \( \rho \) from \( F \) again. Since an \( M \)-dimensional basis for density functions, \( \rho \), implies a choice for the reproducing kernel,
\[ \hat{\rho}(x) = \int dx' \delta(x, x') \hat{\rho}(x'), \] (17)
we can make use of the fact that the span of \( \delta(q, s; q', s') \) traces out the \( M \)-dimensional Hilbert space, \( H^{conf} \), and write its orthonormal basis as \( \{ Y_i \}_1^M \). Eq. 16 is then proved directly by writing the reproducing kernel as the resolution of identity,
\[ \delta(q, s; q', s') = \sum_{i=1}^{M} Y_i(q, s) Y_i(q', s') =: u^\dagger(q, s) f(q', s'). \] (18)
Substituting Eq. 18 into Eq. 16 and comparing to $\phi^i f$ gives the identifications,

$$f(q, s) = AY(q, s) \quad (19)$$

$$u(q, s) = A^{-1}Y(q, s) \quad (20)$$

$$\phi(r) = \int dqds u(q, s)\Phi(x), \quad (21)$$

for any invertible, $M \times M$ matrix, $A$.

To find $\rho$ from $F$, insert Eq. 18 into Eq. 17 to find,

$$\hat{\rho}(x) = \int dx' \delta(r, r')u^\dagger(q, s) f(q', s') \hat{\rho}(x') = u^\dagger(q, s) \hat{F}(r). \quad (22)$$

The last step follows from Eq. 6 and the fact that $\hat{F}_i(r) \in \mathcal{H}^{trs}$, the Hilbert space of functions with reproducing kernel, $\delta(r, r')$.

The above considerations show formally how OZ theory on density space corresponds exactly to a “molecular OZ” theory on moment space because both are built on the same perturbation expansion of log $Z$, and an invertible linear transformation to moment space can be constructed for any space of density functions which admits a convergent basis expansion.

The isomorphism is exhibited by the change of basis in Eqns. 19-20. In this representation, convolution is represented as matrix multiplication in the operator algebra over $\mathcal{H}^{trs} \otimes \mathcal{H}^{conf}$ generated by,

$$(C \ast R)(r, r') \equiv \int dx'' C(r, r'') R(r'', r'), \quad (23)$$

which is isomorphic to,

$$(c \ast \rho_2)(x, x') \equiv \int dx'' c(x, x'')\rho_2(x'', x'), \quad (24)$$

when $c$ is an energy-type function and $\rho_2$ is a density-type function,

$$c(x, x') = f(q, s)^\dagger C f(q', s') \iff C = \int dqds \int dq' ds' u(q, s)u^\dagger(q', s')c(x, x') \quad (25)$$

$$\rho_2(x, x') = u(q, s)^\dagger R u(q', s') \iff R = \int dqds \int dq' ds' f(q, s)f^\dagger(q', s')\rho_2(x, x'). \quad (26)$$

Note how the result of Eq. 23 is of ‘mixed type.’ In the reproducing kernel Hilbert space context, we can cheat and insert the change of basis $f(q, s) = (AA^\dagger) u(q, s)$. However, the difference in types will likely be important for convergence of inner-products between energy-type and density-type functions.

The inner product can be extended to operators by defining a star operation which takes the conjugate-transpose of each matrix and interchanges source and destination points (i.e. $R^*_i(r, r') = R_{ji}(r', r)$ and $\rho_2^*(x, x') = \rho_2(x', x)$), and a trace operation,

$$\text{tr} [C] = \frac{1}{V} \int dr \sum_{i=1}^M C_{ii}(r, r), \quad \text{tr} [c] = \frac{1}{V} \int dx \ c(x, x) \quad (27)$$

so that

$$\text{tr} [C^* \ast R] = \text{tr} [c^* \ast \rho_2]. \quad (28)$$
Symmetry on interchanging source and destination points makes all pairwise operators selfadjoint, satisfying $C = C^*$. These extensions are helpful when formulating a complete theory using $U_2$ from Eq. 13. Treating multi-component solutions by adding an index for each molecule type is a trivial extension.

Working in moment space usually simplifies the energy expressions considerably. For pair energy functions of the form,

$$U_2(x, x') = f(q, s) \mathcal{U}_2(r, r')f(q', s'),$$

the average pair interaction energy is,

$$U_{\text{pair}} = \frac{1}{2} \left\{ \sum_{i,j=1}^{n} U_2(x_i, x_j) \right\} \sim \frac{V}{2} \text{tr} \left[ \mathcal{U}_2 \ast (R \ast H \ast R + F(r)F^\dagger(r')) \right],$$

where we have used the traditional total correlation function,

$$h(x, x') \equiv \frac{\left\langle \sum_{i,j=1}^{n} \delta(x_i, x_j)\delta(x'_i, x'_j) \right\rangle \rho(x)\rho(x')}{\rho(x)\rho(x')} - 1,$$

$$(R \ast H \ast R)(r, r') \equiv \int dq ds \int dq' ds' \rho(x)h(x, x')\rho(x')f(q, s)f^\dagger(q', s').$$

It must be noted that $h$ is not in $\mathcal{H}^{\text{trs}} \otimes \mathcal{H}^{\text{conf}}$, but $\rho(x)h(x, x')\rho(x')$ is. This makes it more natural to treat $R \ast H \ast R$ as a single entity as in Eq. 32, where $R$ is some matrix (discovered below) representing the single-particle density.

Finally, to relate Eq. 4 to Eq. 8, we define the field-field correlation function as,

$$Q(r, r') = \frac{\delta F(r)}{\delta \rho(r')} = \left\langle \Delta \hat{F}(r)\Delta \hat{F}^\dagger(r') \right\rangle = (R \ast H \ast R)(r, r') + R(r, r')$$

identifying the self-terms,

$$\rho_2(x, x') \equiv \sum_{j=1}^{n} \delta(x, x_j)\delta(x'_i, x'_j) \equiv (\Delta \hat{\rho}(x)\Delta \hat{\rho}(x')) - \rho(x)h(x, x')\rho(x')$$

$$R(r, r') \equiv \int dq ds \int dq' ds' \rho_2(x, x')f(q, s)f^\dagger(q', s').$$

In our notation, the rows of $Q$ correspond to the numerator and the columns to the denominator. These are density-type functions, so Eq. 26 applies to transform between $Q$, $R \ast H \ast R$, and $\langle \Delta \hat{\rho}(X)\Delta \hat{\rho}(X')\rangle \hat{F} \cdot \rho^2 \hat{h}, \rho_2$. Using this transformation in Eq. 8 verifies that the response of the field vector is the average of the density response to the corresponding potential and vice-versa that the density response to a perturbation can be expanded in basis of functions whose coefficients depend linearly on the field response at each point.

It should also be noted that $Q(r, r')$ is related to the structure factor probed by electron and neutron scattering experiments. Because each of those experiments probes a single type of density (electric or atomic), each provides one linear constraint on the Fourier transform, $\int e^{-ik \cdot (r-r')}Q(r, r')drdr'$ for each measured wavevector, $k$. 
4 Useful Basis Expansions

Any of the relations in Eq. 18, 19, or 21 could be used to derive a choice for the basis expansion to be used in a numerical or theoretical perturbation theory. However, it is usually unnecessary to start from the eigendecomposition of identity in Eq. 18. Instead, most kernels are derived physically by decomposing the interaction energy expression using Eq. 16. This leads to a set of ‘important’ moments, \( f \), which are the first few terms of an expansion of the interaction energy. Next, these moments are used to find appropriate kernels, \( \delta \), by writing \( \rho \) in the form of Eq. 22.

The obvious basis for a dipole is,

\[
f_{\text{dip}}(q, s) = \left[ \frac{1}{q \mu(s) \bar{q}} \right], \tag{36}
\]

where \( q \in SO(3) \) is treated as a quaternion to rotate the dipole moment, \( \mu(s) \), of the molecule in a reference orientation with internal coordinates, \( s \). In this basis, it is possible to express both electrostatic and isotropic interactions up to dipolar order. It has been investigated extensively for rigid molecules (where \( \mu \) is a fixed axis).\[24\]

We show here that a systematic approach for other situations can be based on finding a quadrature rule for Eq. 18, where \( \delta \) is the reproducing kernel for a class of functions on ‘important’ or ‘coarse-grained’ sub-spaces of \( SO(3) \times S \). In that case, all integrals over the coarse-grained space including Eq. 16 and Eq. 6 can be written as sums over quadrature points, \( \xi_i \in SO(3) \times S \), and we only ever need to know the values of the densities, \( \rho \), and interaction energies, \( \Phi \), at those points.

Specifically, assume we are given an \( M \)-dimensional Hilbert space of functions on \( SO(3) \times S \) with reproducing kernel \( \delta(q, s; q', s') \) and an \( M \)-point quadrature rule for the space. That quadrature rule should have weights \( w_i \) at points \( \xi_i = (q_i, s_i) \) for which,

\[
\delta(q, s; q', s') = \sum_i w_i \delta(q, s; \xi_i) \delta(\xi_i; q', s'). \tag{37}
\]

In this case, choose

\[
f_{r,k}^i(q, s) = w_i \delta(q, s; \xi_i) \quad \text{and} \quad u_{r,k}^i(q, s) = \delta(q, s; \xi_i), \tag{38}
\]

so Eq. 18 is automatically satisfied. The next two equations (21 and 19) identify \( \phi_n(r) \) and \( f_n \) as weighted sums of the external potential \( \Phi(r, \xi_i) \) and the density operator, \( \hat{\rho}(r, \xi_i) \), respectively, evaluated at those quadrature points.

This idea leads to a physically useful basis for full multipolar moment expansion up to order \( T = \sqrt{M} - 1 \) using the equivalent point charge representation,\[36\]

\[
f_{s}^{pc}(q, s) = w_i \int_{y \in \mathbb{R}^3} d\rho^{ch}(y; s) K(\xi_i, qy\bar{q}), \tag{39}
\]

where \( \xi_i \in S^2 \) are Lebedev or other useful\[1\] quadrature points on the unit sphere, \( S^2 \), for polynomials up to order \( T \) and \( K \) is the reproducing kernel defined in Ref. [36], taking a position vector in the laboratory frame \( qy\bar{q} \in \mathbb{R}^3 \), and charge distribution, \( d\rho^{ch}(y; s) \) in a reference frame, to find an equivalent point charge, \( f_{s}^{pc} \), at point \( \xi_i \), fixed in the laboratory frame.

We note here that for \( T = 1 \), the reproducing kernel is \( K(x, y) = (1 + 3x \cdot y) \). It can be integrated with four quadrature points at the vertices of a tetrahedron inscribed in a unit sphere. These are related to the
choice of basis in Eq. 36 by the matrix,

\[
    f^{pc,1}(q, s) = \frac{1}{4} \begin{bmatrix}
        1 & 0 & 0 & 3 \\
        1 & \sqrt{8} & 0 & -1 \\
        1 & -\sqrt{2} & \sqrt{6} & -1 \\
        1 & -\sqrt{2} & -\sqrt{6} & -1 
    \end{bmatrix} f^{\text{dip}}(q, s).
\]

The resulting moments describe the effective point charge placed at each vertex. The first column distributes the total charge evenly among the four points. The last three are row-vectors of the vertex locations. It can be checked that they sum to zero since a dipole should not contribute to the total charge.

For rigid molecules, it may make sense to choose instead

\[
    f^{\text{rot}}(q, s) = \frac{1}{12} K_R(q_i, q),
\]

where \(q_i\) are the 12 Hurwitz quaternions\(^{[26]}\) (modulo an overall sign, which express two rotations to each of the vertices of an octahedron) and

\[
    K_R(q, q') = \sum_{j=0}^{5} (j + 1) U_j(q \cdot q'),
\]

is the reproducing kernel for the set of polynomial functions on the unit quaternions with degree less than 6. The scalar product between quaternions is,

\[
    q \cdot q' \equiv (qq' + q'q)/2,
\]

and \(U_j\) is the \(j^{th}\) order Chebyshev polynomial of the second kind,

\[
    U_0(z) = 1, \quad U_1(z) = 2z, \quad U_j(z) = 2zU_{j-1}(z) - U_{j-2}(z).
\]

The reproducing property of Eq. 42 is a consequence of the zonal expansion\(^{[9]}\) and the Funk-Hecke formula. For working with Eq. 43, it is helpful to have the geometric identities,

\[
    a \cdot b = (ac) \cdot (bc) = (ca) \cdot (eb),
\]

for any normalized quaternion \(c\) (i.e. \(cc = 1\)). These express invariance of \(K\) to the choice of laboratory orientation frame.

The dipole representation has only recently been investigated in the literature in the case of rigid molecules. Our generalizations to multipolar distributions with flexible molecules and over the quaternion algebra have not been investigated before for density functional theories. These have the potential to offer order of magnitude computational savings over straightforward tensor products of angular grids.\(^{[16]}\)
4.1 Translational Basis

By writing most of our results as functions of \( r, r' \) we have been able to avoid the question of a translational basis. However, extension of the matrix formulation to \( \mathcal{H}^{\text{trs}} \) is indispensable for numerical work.

The simplest translational basis to implement is the 3D Fourier basis on a regularly spaced grid representing a periodic cube with lattice spacing \( L \) (so \( \Omega_1^{\text{FT}} = [0, L]^3 \times \text{SO}(3) \times \mathbb{S} \)). This case (for arbitrary 3D lattices) along with a fast and accurate numerical approximation for low-wavevector modes was discussed by Essman et. al.,\cite{essman} and additional results are available in Ref. \cite{williamson}. It corresponds to a reproducing kernel that is ‘band-limited’ by truncation at a cutoff \( K_{\text{max}} \), so that the reproducing kernel is,

\[
\delta_{\text{FT}}(r, r') = \frac{1}{K_{\text{max}}^3} \sum_{k_1, k_2, k_3=1}^{K_{\text{max}}} e^{2\pi i k \cdot (r-r')/L}.
\]

Note that this is a smooth analytic function of \( r \) and \( r' \), but its use in numerical evaluations of \( - \log Z[\phi] \) implies the projection of pair energy functions via \( \phi(r) = -\beta \int \delta(r, r')U(r')dr' \).

The traditional basis for the OZ equations has been the spherical Bessel function expansion. We provide a new formula for the expansion here that resolves the long-standing, open question on how to properly treat the origin. Our answer is based on the simple analogy between the discrete Fourier transform on the torus and the Fourier-Bessel series for functions on finite intervals. The spherical Bessel function method is usually supplemented by the condition that the functions concerned (e.g. \( h(r) \)) have finite range \( R_{\text{max}} \), so \( \Omega_1^{\text{SB}} = ([0, R_{\text{max}}] \times \mathbb{S}^2) \times \text{SO}(3) \times \mathbb{S} \). Adding the condition that \( h(r > R_{\text{max}}) = 0 \) with \( h \) continuous at \( R_{\text{max}} \) is exactly the prerequisite for applying the Fourier-Bessel series.

Truncating the series at \( N_{\text{max}} \) and using a spherical harmonic expansion over directions, \( r \in \mathbb{S}^2 \) leads to the general expression,

\[
h(r) = \sum_{n=1}^{N_{\text{max}}} \sum_{l=0}^{L_{\text{max}}} \sum_{m=-l}^{l} C_{n,l,m} h_{n,l,m}(r), \quad h_{n,l,m}(r) \equiv j_l(|r| z_{n,l}/R_{\text{max}}) Y_l^m(r),
\]

where \( z_{n,l} \) is the \( n^{th} \) smallest root of \( j_l(z) \) (not counting roots at \( z = 0 \)). For real \( h \), the coefficients obey \( C_{n,l,m} = C_{n,\bar{l},-m} \) so that each \( n,l \) has only \( 2l+1 \) associated parameters. The normalization of the spherical harmonics is \( \int_{\mathbb{S}^2} dr Y_l^{m'}(r) Y_l^m(r) = \delta_{l,l'} \delta_{m,m'} \).

Functions in this Hilbert space have the Fourier transform,

\[
\hat{h}_{n,l,m}(k) = 4\pi R^3 i^{-l} Y_l^m(k) \int_0^1 x^2 dx j_l(|k|R) j_l(x z_{n,l})
\]

\[
= 4\pi R^3 i^{-l} Y_l^m(k) |k|R j_{l-1}(|k|R) j_l(z_{n,l}) - z_{n,l} j_{l-1}(z_{n,l}) j_l(|k|R)\frac{z_{n,l}^2 - |k|R^2}{z_{n,l}^2}.
\]

On shells where \( R|k| = z_{n',l} \), this reduces to zero if \( n \neq n' \) or (for \( n = n' \))

\[
\hat{h}_{n,l,m}(k z_{n,l}/R) = 2\pi R^3 i^{-l} Y_l^m(k) \left( j_l(z_{n,l})^2 - j_{l-1}(z_{n,l}) j_{l+1}(z_{n,l}) \right).
\]

Each of the \( h_{n,l,m} \) are mutually orthogonal, with normalization

\[
N_{n,l,m} = \int dr h_{n,l,m}(r) h_{n',l',m'}(r) = \delta_{n,n'} \delta_{l,l'} \delta_{m,m'} 2\pi R^3 j_{l-1}(z_{n,l})^2.
\]
The \( l = 0 \) case makes use of \( j_{-1}(z) = \cos(z)/z \). The associated reproducing kernel is therefore

\[
\delta_{SB}(r, r') = \sum_{n=1}^{N_{\text{max}}} \sum_{l=0}^{L_{\text{max}}} \sum_{m=-l}^{l} \frac{h_{n,l,m}(r)h_{n,l,m}(r')}{N_{n,l,m}}.
\]  

Note that although the spherical Bessel function basis makes physical sense for smooth radial functions with limited range, it is not closed under convolution or multiplication of functions. Nevertheless, Eq. 49 shows that the coefficients can be visualized as momentum shells, and so convolution of \( h \) and \( h' \) can be projected back to the Hilbert space (Eq. 47) by computing the values of \( \tilde{h}_{n,m} \tilde{h}_{n,m}' \) on those shells using Eq. 48 (which has the same form as the ‘SB’ reproducing kernel in Fourier space).

## 5 Transformation of OZ and DFT

This section derives the well-known connection between correlation functions and effective Green’s functions for field theories. The statement leads to both an OZ equation defined directly in matrix space and a corresponding DFT.

The Legendre transform pair for \( \log Z[\phi] \) is,[18]

\[
\mathcal{S}[F] \equiv \inf \phi \left[ \log Z[\phi] - \langle \phi, F \rangle \right]
\]

\[
- \log Z[\phi] = \inf_F \left[ -\mathcal{S}[F] - \langle \phi, F \rangle \right]
\]

The notation \( \mathcal{S} \) emphasizes that density functionals are generalized entropies. Because of the exponential function in Eq. 1, \( \log Z \) is convex and lower-semicontinuous, while \( \mathcal{S} \) is concave and upper-semicontinuous. The second equality holds at least when \( \phi \) is bounded.[12] In this paper, the spaces of \( \phi \) and \( F \) are both \( \mathcal{H}_{\text{trs}} \otimes \mathcal{H}_{\text{conf}} \). The functional derivatives of \( \log Z \) and \( \mathcal{S} \) are well-defined in the finite-basis case, but require some technical proofs of convergence with basis size.

### 5.1 OZ Equation

Eq. 33 is related to the second derivative of \( \mathcal{S} \) by the thermodynamic conjugate relationship,

\[
\frac{\delta \phi(r)}{\delta F(r')} = Q^{-1}(r, r') = - \frac{\mathcal{S}'[F]}{\delta F(r) \delta F(r')}.
\]

The inverse indicated above is the inverse under convolution in the operator algebra on \( \mathcal{H}_{\text{trs}} \otimes \mathcal{H}_{\text{conf}} \), where \( I \delta(r, r') = Q * Q^{-1} \). So we see that \( Q^{-1} \) is the effective Green’s function for the field theory. In particular, the inverse of the correlation function is the effective interaction energy in the Gaussian approximation for the probability of a given field configuration, \( F \),

\[
\log P[F] \approx \mathcal{S}[F] \approx -\frac{1}{2} \int dr dr' F(r) F(r') Q^{-1}(r, r').
\]

However, \( \delta(r, r') \) is not necessarily diagonal in translation or conformation space. Hence, \( \delta(x, x')u(x') \neq u(x)\delta(x, x') \) in general, and we can only write \( \rho_2(x, x') \sim \delta(x, x')\rho(x) \) in the limit of an infinite basis size.
To avoid assuming the limit, use the definitions in Eq. 33 to find that the equation \( Q^{-1} \ast Q = I \delta \) is solved by a pair of operators, \( R^{-1} \) and \( C \), that satisfy,

\[
H - C = H \ast R \ast C,
\]

so that

\[
Q^{-1} = R^{-1} - C. \tag{57}
\]

Note that \( Q, H, \) and \( R \) are all operators on \( \mathcal{H}^{\text{trs}} \otimes \mathcal{H}^{\text{conf}} \). Thus, their inverses are formally defined while their existence depends on whether \( R \) is invertible. Since \( R \) is a 1-particle quantity, its is invertible iff. every function in the Hilbert space has a nonzero overlap with \( \rho(x) \).

Comparing to the OZ equation shows finally that since \( R, Q \) were defined as moments (as in Eq. 19), then \( R^{-1} \) and \( C \) are energy-type functions, whose translation to \( \rho_2^{-1} \) and \( c \) follows Eq. 25. We note again that the convolution, \( R \ast H \ast R \), rather than direct multiplication, is required to maintain consistency with the use of the total correlation function, \( h \), in the OZ equation because \( \delta(r, r') f(r') \neq f(r) \delta(r, r') \) for finite \( \mathcal{H}^{\text{trs}} \).

### 5.2 Density Functional

The density functional minimization procedure to determine \( \beta \mu^{\text{ex}}[\phi] \) is given in Eq. 53. It often makes use of a more explicit form for \( S[F] \) derived from integrating Eq. 54 along the path \( F_\lambda = F_0 + \lambda(F - F_0) \) from \( F_0 = 0 \) to \( F = F[\phi] \) and making an assumption for the path-dependence of \( Q^{-1}[F_\lambda] = Q_\lambda^{-1} \). The functional derived in this section therefore assumes at least that \( S[F_\lambda] \) is an analytic function of \( \lambda \) along this path. The assumption is valid when the path does not cross a phase transition.

The integral from \( F_0 \) (where the entropy of solvation is \( S[F_0] = 0 \)) is,

\[
S[F] = -\int_0^1 (1 - \lambda) d\lambda \left\langle F - F_0, Q_\lambda^{-1} \ast (F - F_0) \right\rangle, \tag{58}
\]

which uses the inner product from Eq. 7. Inserting Eq. 57 decomposes this into ideal and excess parts,

\[
S[F] = \left\langle F - F_0, (S^{\text{id}} + C/2) \ast (F - F_0) \right\rangle \tag{59}
\]

\[
C \equiv 2 \int_0^1 (1 - \lambda) d\lambda \ C_\lambda \tag{60}
\]

\[
S^{\text{id}} \overset{\text{lin}}{=} R_0^{-1/2} \ast (I - (M^{-1} + I) \ast \log(I + M)) \ast M^{-1} \ast R_0^{-1/2} \tag{61}
\]

\[
M \overset{\text{lin}}{=} R_0^{-1/2} \ast (R_1 - R_0) \ast R_0^{1/2}. \tag{62}
\]

Subscripts indicate the value of \( \lambda \) at which each variable is evaluated. Note that Eq. 61 requires a further assumption to compute the 1-particle correlations, \( R \) from the local field, \( F \). The linear assumption is indicated by the label ‘lin’ above, and is removed in Eq. 64.

The ideal term presents a conceptual difficulty in the basis-set expansion, since Eq. 22 describes a projected density corresponding to a given average \( F(r) \). That projected density does not match the (known) maximum entropy form expected for an ideal gas using a finite basis for \( \mathcal{H}^{\text{conf}} \). Nevertheless, assuming \( R_\lambda = R_0^{1/2} \ast (I + \lambda M) \ast R_0^{1/2} \) is a linear function of \( \lambda \), its inverse can be integrated to find \( S^{\text{id}} \). Eq. 61 is derived from the spectral theory of matrices using the integral \( \int_0^1 (\lambda - 1)/(1 + \lambda) d\lambda = (1 - (t^{-1} + 1) \log(1 + t))/t. \)
The result has a removable singularity at zero. When an eigenvalue, $t$, of $M$ approaches zero, the associated projection in $S^{id}$ can still be found from its series expansion, $\sum_{n=0}^{\infty} (-1)^n t^n / (n + 1)(n + 2)$.

As noted in Ref. [34], it makes sense to treat the single-molecule term specially. In particular, in the limit where the basis exactly describes the density function, the single-molecule term must go to,

$$S_{id}[F] \equiv \left\langle F - F_0, S^{id} * (F - F_0) \right\rangle$$

$$\sim \int dx \left( \rho_1(x) - \rho_0(x) - \rho_1(x) \log \frac{\rho_1(x)}{\rho_0(x)} \right).$$

(63)

This entropy is exactly known when the 1-particle density function, $\rho(x)$ is also known, but is incompletely determined by only the spatial, 1-particle moments, $F(r)$.

Maximizing the entropy given a few known moments of a distribution is a traditional problem in statistical mechanics. Assume $f$ has been chosen so that $F(r)$ is sufficient to determine the particle number density, $n(r)$, then solve the maximum entropy problem over the remaining, internal, coordinates to find the conditional probability, $P(q, s| r)$ in $\rho(x) = n(r)P(q, s| r)$. Applying this procedure to Eq. 63 shows that,

$$S_{id}[F] \sim \int dr \left\{ n(r) - n_0(r) + n(r) \left[ S^{conf}(F(r)) - S^{conf}(F_0(r)) \right] \right\}$$

$$S^{conf}(F(r)) \equiv -\log n(r) + \inf_{\phi_k} \left[ \log \int e^{i\phi_k F(r)} d\mu_1(q, s) - \phi_k \right].$$

(64)

In the last equation, we choose $d\mu_1(q, s)$ to be a probability distribution over single-molecule conformations in an ideal gas (a canonical, 1-molecule ensemble as $V \rightarrow \infty$). That single-molecule ensemble has average $F(r)/n(r) = \int P(q, s| r) f(q, s) dq ds$. The limits should be equal because as the basis size grows, $F_\lambda$ completely determines $\rho_\lambda(x)$ at each $\lambda$. The result will be the only solution of the maximum entropy distribution, $P_\lambda(q, s| r) dq ds \sim e^{\phi_k F_\lambda} / \int e^{\phi_k F_\lambda} d\mu_1$. Aside from the constant offset contributed by $S^{conf}(F_0(r))$, this is an upper bound to the actual entropy that converges to $S_{id}$ in the limit.

6 Application to the Dipolar Fluid

In this section, we compare our results with the traditional expansion of the OZ equation into rotational invariants. The rotational invariant basis functions[8] are given in Table 1. Each row of the table also lists the angular integral part of its 3D Fourier transform in the form,

$$\int_{S^2} e^{-ik \cdot r} d\Phi_T(r, \mu, z) = 4\pi \Phi_T(k, \mu, z) J_T(|r||k|).$$

(65)

The notation $r$ denotes a unit vector on $S^2$, the surface of a sphere in 3D.
Using the choice of $f_{\text{dip}}$ from Eq. 36,

\[ h(x, x') = \left[ \frac{1}{m' q' \hat{q}} \right]^T \begin{bmatrix} h_J, & r_{hp} \\ -r_{hp}, & 3h_D \otimes r + I(h_\Delta - h_D) \end{bmatrix} \left[ \frac{1}{m' q' \hat{q}} \right] \tag{66} \]

\[ C(r, r') = \left[ \begin{array}{c} c_I, \\ r_{cp} \\ -r_{cp}, 3c_D \otimes r + I(c_\Delta - c_D) \end{array} \right]. \tag{67} \]

where $r$ is a unit vector in the direction $r$, $m$ is the magnitude of the molecular dipole, and $H(r, r') = H(r - r')$ and $C(r, r') = C(r - r')$ are translationally invariant. Note that taking the integral of Eq. 26 multiplies the inner matrix of Eq. 66 by the diagonal factor, $B = \text{diag}(1, m^2/3, m^2/3, m^2/3)$, on both sides. This matches the self-correlation function in a uniform system ($R(r, r') = \left(\frac{H}{\bar{L}}\right) \delta(r, r')B$), leaving $H$ as the inner matrix in Eq. 66. The complementary function to $f$ is $u = fB^{-1}$.

If we define the Fourier-Bessel transforms according to Eq. 65,

\[ \tilde{c}_T(|k|) \equiv 4\pi \int_0^\infty |r|^2d|r| \ J_T(|r||k|)c_T(|r|), \tag{68} \]

then the Fourier transforms of Eqs. 66-67 are the same, replacing $r$ with $k$, and each $h_T$ with $\tilde{h}_T$ (and $c_T$ with $\tilde{c}_T$). There is an essential symmetry here that interchanging source and destination molecules (the star operation of Eq. 28) leads to the same interaction energy. Because of this, the Fourier transform, $\tilde{C}$, is Hermitian.

It can be noticed immediately that the lower-right block decomposes into a component, $\tilde{c}_L \equiv \tilde{c}_\Delta + 2\tilde{c}_D$ in the direction $k \otimes k$ and $\tilde{c}_L \equiv \tilde{c}_\Delta - \tilde{c}_D$ along its orthogonal complement, $I - k \otimes k$. These two components are scaled versions of $c_+$ and $c_-$ in Wertheim’s original solution of the MSA for the dipolar fluid.\[43\] The matrix notation of Eq. 56 has thus led us directly to the three decoupled OZ equations given in that work (when $c_p = 0$). The particular choice of scale used there was,

\[ \tilde{h}_L = 6K'\tilde{h}_+ \tag{69} \]

\[ \tilde{h}_T = -3K'\tilde{h}_- \tag{70} \]

\[ K' = \int_0^\infty \frac{dx}{x} h_D(x). \tag{71} \]

That scale was chosen to make the coefficient of $h_D$ be $1/3K'$, so that $h_+(0) = h_-(0) = -1$. We can summarize Wertheim’s process of finding these boundary conditions by noting that he found a general relation between spherical Bessel transforms of orders 2 and 0,

\[ -\int_0^\infty x^2dxj_2(kx)f(x) = \int_0^\infty x^2dxj_0(kx)f(x) = \text{SBT}_0[f](x) = \text{SBT}_2[f](k) \tag{72} \]

\[ \tilde{f}(k) \equiv f(x) - 3\int_x^\infty \frac{dy}{y}f(y) = \text{SBT}_{-1}^{-1}[\text{SBT}_2[f]](x). \tag{73} \]

Eq. 72 can be verified by substituting for $f$, interchanging the integrals and integrating by parts. The last parts of Eqs. 72 and 73 use $\text{SBT}_n$ as shorthand for the spherical Bessel transform of order $n$ using $J_T$ from Table 1. Thus,

\[ h_+ = \frac{2}{6K'}\text{SBT}_{-1}^{-1}[\text{SBT}_2[h_D]] + \frac{1}{6K'}h_\Delta, \tag{74} \]

and $h_+(r) = -1$ for $r$ within the excluded volume region, since $h_D(r) = h_\Delta(r) = 0$ there.
The corresponding MOZ equations (56) read
\[ \begin{align*}
\tilde{h}_+ - \tilde{c}_+ &= 2K' \rho m^2 \tilde{h}_+ \tilde{c}_+ \\
\tilde{h}_- - \tilde{c}_- &= -3K' \rho m^2 \tilde{h}_- \tilde{c}_- .
\end{align*} \] (75) (76)
They differ from Wertheim’s result because here \( c \) should scale as \( \beta/4\pi\varepsilon_0 r^3 \), rather than \( \beta m^2/4\pi\varepsilon_0 r^3 \).

6.1 Casimir Energy for Polarizable Point Dipoles

Adapting the last section to the case of a gas of polarizable point dipoles only requires using \( f = [1, \mathbf{p}]^T \) (where \( \mathbf{p} \) is now the 3-dimensional point-dipole vector on each atom) and specifying the default distribution over \( \mathbf{p} \). For the latter, we assume the Gaussian measure
\[ ds = (2\pi\sigma^2)^{-3/2} e^{-|\mathbf{p}|^2/2\sigma^2} d\mathbf{p}, \] (77)
associated with polarizability \( \alpha = \beta\sigma^2 \). The integral \( B = \int \mathcal{I} f \mathcal{I} ds = \text{diag}(1, \sigma^2, \alpha^2) \) differs, while the rest of the analysis remains unchanged. In particular, the definition of \( h_\pm \) and \( c_\pm \) should be the same as Eqns. 69 and 70, since the numerical factors are associated with the Fourier transform over \( r \).

However, the appearance of \( R \) in Eq. 56 now requires,
\[ \begin{align*}
h_+ - c_+ &= 6K'\sigma^2 \rho_0 h_+ * c_+ \\
h_- - c_- &= -3K'\sigma^2 \rho_0 h_- * c_-, \end{align*} \] (78) (79)
where \( \rho_0 = \langle n \rangle / V \), with the same boundary conditions on \( h \) and \( c \).

Assuming the hypernetted chain closure (\( \tilde{C} = C \)), the solvation free energy functional contains isotropic and vector parts,
\[ -\log Z[\phi] = \inf_{\phi} \left\{ \mathcal{F}_n[\phi_I] \right. \right. \]
\[ + \inf_{\mathbf{p}} \left. \left. \left[ \int \frac{|P(r)|^2}{2n(r)\sigma^2} \right] \right. \right. \]
\[ \left. - \frac{1}{2} \left\langle \left\langle P, C \mathbf{P} * P \right\rangle - \left\langle \phi_P, P \right\rangle \right. \right. \}
\[ + \left. \left. \left( \mathcal{F}_n[\phi_I] \right) \right. \right. \]
\[ = \int d\mathbf{r} \left\{ \rho_0(r) - n(r) + n(r) \log \frac{n(r)}{\rho_0(r)} \right. \right. \]
\[ \left. - \frac{1}{2} \left\langle \left\langle \rho_0, c_1 * (n - n_0) \right\rangle - \left\langle \phi_I, n \right\rangle \right. \right. \}
\[ \left. \right. \] (80) (81)
The matrix \( C \mathbf{P} \) is the lower-right \( 3 \times 3 \) sub-block of Eq. 67. This form is particularly suitable for computational investigations of implicit solvent.

The \( \mathcal{F}_n \) term describes normal excluded volume interactions between the solute and solvent. The other contribution to the solvation free energy arises from electrostatic fluctuations, and describes a dispersion energy. The inner minimization in Eq. 80 has the solution,
\[ -\frac{1}{2} \left\langle \left\langle \phi_P, (I \delta(r, r')/\sigma^2 n(r) - C \mathbf{P}(r, r'))^{-1} * \phi_P \right\rangle \right. \] (82)

The solvation free energy of a polarizable point dipole is the exponential average of the solvation free energies of each of its possible configurational states (Eq. 15). We would like to use a dipole-dipole interaction energy, \( \phi_P(r) = \partial_r \mathbf{p} \cdot \partial_r \mathbf{p} / 4\pi\varepsilon_0 |\mathbf{r}| \), and integrate \( Z[\phi_I, \phi_P] \) over all possible solute polarizations, \( \mathbf{p} \) using the 1-molecule distribution from Eq. 77. However, \( n(r) \) technically depends on the solute’s polarization. Ignoring this dependence and using \( Z \) instead of \( Z_N \) (which ignores surface effects[4]) yields an estimate of the solvation free energy for a polarizable dipole,
\[ -\log Z[\phi_I] \approx \inf_\mathbf{n} \left\{ \mathcal{F}_n[\phi_I] + \frac{3}{2} \log \left( 1 - q |n| \frac{\beta m^2}{4\pi\varepsilon_0} \right) \right. \} , \] (83)
with

\[ q[n] = \int dr \int dr' \frac{\delta(r, r')}{|r|^3|r'|^3} \left[ \partial_r \otimes \partial_r \left( I \delta(r, r')/\sigma^2 n(r) - C_P(r, r') \right)^{-1} \delta(r, r') \right]. \]  

(84)

This latter expression provides a new route to calculate the classical dispersion energy of solvation. Expanding the Green’s function,

\[ (I \delta(r, r')/\sigma^2 n(r) - C_P(r, r'))^{-1} = \sigma^2 I \delta(r, r') n(r') + \sigma^4 n(r) C_P(r, r') n(r') + O(\sigma^6), \]  

(85)

gives a Hamaker integral and a correlation correction as its first few terms.

7 Discussion

Molecular density functional theory has become a standard technique in the statistical mechanics of fluids, but is not quite as popular as as electronic density functional theory or the Poisson-Boltzmann (or Debye-Hückel theory) for electrolytes. Part of this difficulty is due to a smaller body of literature which does not focus on basis set expansions. Our approach here follows a canonical route\[5\] by developing the theory through the particle insertion expressions (Eqs. 1-4). It contributes a careful discussion of the role of basis functions as decomposing a resolution of identity, \( \delta(x, x') \). It also includes a sketch of free energy convergence issues that are critical for numerical work.\[28,25,23\]

Our presentation of the spherical Bessel translational basis expansions contrasts with standard discussions of fast, grid-based spherical Bessel transformations.\[39,40\] Both provide a Fourier transform method for computing convolutions of range-limited functions and require projection of the result. However, grid-based methods use error analysis based on Riemann summation, and leave some ambiguity on the proper treatment of the origin.\[39\] Using a space of analytical functions identifies three independent sources of error which are understood in the sense of projections – approximating the original functions, and then projecting the result of each multiplication and convolution. It also has the advantage of strong results on numerical integrals.\[20\] Despite these advantages, the basis of spherical Bessel functions has the same Gibbs’ phenomenon issue as the Fourier transform – making it poorly approximate step functions.\[13,25\] Treating hard sphere solvation likely requires re-considering grid-based methods, for example using a Haar basis of piecewise constant radial functions.

The operator algebra of 2-point correlation functions developed from Eq. 23 through Eq. 30 is a central idea of this work. It enables compact expressions like the applications in Sec. 6, and hides the complexities of new conformational information that can be encoded in the basis (Sec. 4). We can go even further to write the density functional of Sec. 5 into a complete minimization problem for a multi-component mixture by adding a species index, \( \alpha \in \{1, 2, \ldots, \nu\} \) to the Hilbert space, \( \mathcal{H} = (\alpha : \{1, \ldots, \nu\}\otimes \mathcal{H}^{\text{conf}}, (\nu \text{ is the number of chemical components}). \) Then the density response at \( x \) for molecules of type \( \alpha \) on inserting a molecule of type \( \gamma \) at \( y \) is \( \rho^{(\gamma, 0)}(\alpha, x) = \rho^0(\alpha, x)(h(\alpha, x; \gamma, y) + 1). \) It has moments \( F^{(\gamma, 0)}(\alpha, r) = \iint f_{\alpha}(q, s) \rho^{(\gamma, 0)}(\alpha, x) dq ds. \) Making these substitutions shows the response function can be replaced by the total correlation function,

\[ \iint F^{(\gamma, x')}(\alpha, r) f_\gamma(q', s') \rho^0(\gamma, x') dq' ds' \sim [R_0 \ast H \ast R_0 + F_0 F_0^\dagger] \rho(\alpha, r; \gamma, x'). \]  

(86)

All minimization problems at once are then expressed by integrating Eq. 53 with weight \( \rho^0(\gamma, y), \)

\[ \sum \gamma \int \beta \mu^\gamma(y) \rho^0(\gamma, y) dy = \inf_{\mathbf{U}} \left[ \beta \mathbf{U}_2 \ast \mathbf{Q} + (\mathbf{Q} - F_0 F_0^\dagger) \ast (S^\text{idd} + \tilde{C}/2) \ast (\mathbf{Q} - F_0 F_0^\dagger) \ast R_0^\dagger \right], \]  

(87)
where $Q \equiv R_0 \ast H \ast R_0 + F_0 F_0^\dagger$. This expression is not as computationally expensive as it appears, since the trace of a pairwise operator over translational and rotational space reduces by symmetry to an evaluation at the origin (with identity rotation). It also enables enforcing the positivity requirement for the spectrum of $Q$. By casting Eq. 87 in the form required for robust numerical convex optimization methods,[10,41] we have created a new path for addressing the thermodynamic stability question in OZ solvers.

Eq. 57 shows that there is no difficulty in principle with numerically computing $c$ at small wave vectors by inverting $Q$ sampled during molecular dynamics simulations. Previous observations had suggested that a fitting procedure was necessary because of excluded volume effects. Standard estimates for the estimation error in the variance-covariance matrix, $Q$, show that the error for $Q^{-1}$ (and hence $C$) is largest for ‘stiff’ modes. Statistical mechanical systems become uncorrelated away from critical points, so low wave vectors should have ideal gas-like fluctuations. Large wave vectors, on the other hand, are energetically unfavorable and will have larger uncertainties. Additionally, a finite Fourier-basis will lead to band-limiting. In real space, this translates to correct long-range features of $c(r)$ with increasing error around the origin and possible high-frequency oscillation.

8 Conclusions

It is clear that this approach can be usefully applied to new problems in analytical and numerical solvation thermodynamics. The concise derivations of Sec. 6 were enabled by translating the OZ equation to moment space. Within this framework, we immediately have Eq. 59 as an approximate expression for the density functional. Extending these results to alternative closures other than the mean spherical approximation is also simplified in the matrix formulation.

The translation to moment space also simplifies analytical and numerical investigations involving specialized forms of interaction energy. Using Eq. 57, direct correlation functions for higher-order multipolar interactions can be now computed straightforwardly from correlations (Eq. 33) calculated in molecular dynamics simulations. Several recent results (and computational implementations)[37] have tackled this inverse problem for dipolar solvents.[24] The present work shows that further results of this type can be made unambiguous by exactly specifying which basis was used for $H^{tr}$ and $f(q, s)$. The complete theory above applies to any such basis.

Section 4 contains a novel presentation of several possible basis expansions using the framework of reproducing kernel Hilbert spaces. This new perspective treats inter- and intra-molecular degrees of freedom in a holistic way. It also provides analytical functional forms that can be smoothly extrapolated to the origin (important for determining macroscopic fluid properties) and are suitable for investigating convergence of approximations.

The formulation of the excess chemical potential using Eq. 15 goes beyond rigid molecule DFT by including intramolecular degrees of freedom on the same footing as molecular orientation. This points out interesting new questions for analysis on the convergence of the test particle insertion method, Eq. 15. In particular, the convergence of Eq. 15 is analogous to the problem of convergence in mean studied in the theory of Orlicz spaces.

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31. Matyushov, D.V., Ladanyi, B.M.: A perturbation theory and simulations of the dipole solvation thermodynamics: Dipolar hard spheres. J. Chem. Phys. 110, 994 (1999). DOI 10.1063/1.478144
32. Mazenko, G.F.: Nonequilibrium Statistical Mechanics. Wiley-VCH (2006)
33. Raineri, F.O., Stell, G.: Dielectrically nontrivial closures for the RISM integral equation. J. Phys. Chem. B 105(47), 11880–11892 (2001). DOI 10.1021/jp0121163
34. Ramirez, R., Gebauer, R., Mareschal, M., Borgis, D.: Density functional theory of solvation in a polar solvent: Extracting the functional from homogeneous solvent simulations. Phys. Rev. E 66, 031206 (2002). DOI 10.1103/PhysRevE.66.031206
35. Rao, M.M., Ren, Z.D.: Theory of Orlicz spaces, Monographs and textbooks in pure and applied mathematics, vol. 146. M. Dekker, New York (1991)
36. Rogers, D.M.: Real-space quadrature: a convenient, efficient representation for multipole expansions. J. Chem. Phys. 142, 074101 (2015)
37. Rogers, D.M.: Extension of Kirkwood-Buff theory to the canonical ensemble. J. Chem. Phys. 148, 054102 (2018). DOI 10.1063/1.5011696
38. Sluckin, T.J.: Density functional theory for simple molecular fluids. Mol. Phys. 43(4), 817–849 (1981). DOI 10.1080/00268978100101711
39. Talman, J.D.: NumSBT: A subroutine for calculating spherical Bessel transforms numerically. Comput. Phys. Commun. 180(2), 332–338 (2009). DOI 10.1016/j.cpc.2008.10.003
40. Toyoda, M., Ozaki, T.: Fast spherical Bessel transform via fast Fourier transform and recurrence formula. Comput. Phys. Commun. 181, 277–282 (2010). DOI 10.1016/j.cpc.2009.09.020
41. Tuncel, L.: Interior Point Methods for Semidefinite Programming, pp. 1679–1683. Springer, Boston, MA (2008). DOI 10.1007/978-0-387-74759-0
42. Vrbka, L., Lund, M., Kalcher, I., Dzubiella, J., Netz, R.R., Kunz, W.: Ion-specific thermodynamics of multicomponent electrolytes: A hybrid HNC/MD approach. J. Chem. Phys. 131, 154109 (2009)
43. Wertheim, M.S.: Exact solution of the mean spherical model for fluids of hard spheres with permanent electric dipole moments. J. Chem. Phys. 55, 4291 (1971). DOI 10.1063/1.1676751
44. Zhao, S., Liu, H., Ramirez, R., Borgis, D.: Accurate evaluation of the angular-dependent direct correlation function of water. J. Chem. Phys. 139, 034503 (2013)