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Citation: The Journal of Chemical Physics 39, 474 (1963); doi: 10.1063/1.1734272
View online: https://doi.org/10.1063/1.1734272
View Table of Contents: http://aip.scitation.org/toc/jcp/39/2
Published by the American Institute of Physics

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Equation of State for Hard Spheres*†

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(Received 25 March 1963)

Simple and exact expressions have been found for the compressibility and pressure equations of state predicted by the Percus–Yevick equation for hard spheres. The equations of state are in good agreement with the machine calculations of Wainwright and Alder, and Wood, Parker, and Jacobson.

INTRODUCTION

The system consisting of hard-sphere molecules is a convenient model for the initial study of the behavior of dense gases and liquids. One usually hopes that this model will exhibit most of the salient features of a real system. Also, since the mathematical treatment of this model is relatively simple, it is often used to test approximate theories.

The Percus and Yevick equation (1) is one of the more recent approximate integral equations for the determination of the radial distribution function of a fluid. Percus and Yevick1 pointed out that their equation leads to much better results for the fourth virial coefficient of a hard-sphere gas than earlier theories based on the Kirkwood superposition approximation.2 Recently Rushbrooke3 calculated the fifth and sixth virial coefficients using the Percus–Yevick equation. The fifth virial coefficient is in reasonably good agreement with the Monte Carlo estimate.4 The exact sixth virial coefficient is unknown. The fact that the first six virial coefficients can be fitted by a simple formula suggested that the exact equation of state, predicted by the Percus–Yevick equation, may be a simple expression. This is indeed true, and in this paper we calculate the exact Percus–Yevick equation of state.

The calculation proceeds in several steps. Taking the unit of length equal to the diameter of the sphere, we first show that the radial distribution function is piecewise analytic with discontinuities in the derivatives at \( r = 2, 3, 4, \ldots \). The Laplace transform of the radial distribution function is then obtained in terms of a function \( h_0(r) \) defined for \( 0 < r < 1 \). A set of sufficient conditions such that \( g(r) \) is piecewise analytic in the manner described are then found, which completely determine the function \( h_0(r) \). It is then shown that the equations of state can be easily calculated from the function \( h_0(r) \).

FUNCTION \( h_0(r) \)

The Percus–Yevick equation may be written in the following form:\n
\[
\tau(x) = 1 + n \int \{ \exp[-\theta V(y)] - 1 \} \tau(y) \times \{ \exp[-\theta V(x-y)] \tau(x-y) - 1 \} dy, \tag{1}
\]

where \( n \) is the number density, \( V \) the two-body potential, \( \theta = 1/kT \), and

\[
\tau(x) = \exp[\theta V(x)] g(x),
\]

where \( g(x) \) is the radial distribution function. In the case of singular potentials such as the hard sphere potential, it is necessary to solve first for \( \tau(x) \) rather than directly for \( g(x) \).\n
From the definitions of \( h(r) \) and \( \tau(r) \) one has for hard spheres of a general relation due to Broyles.5

\[
h(r) = r - 2\pi na^3 \int_0^1 h(s) ds \int_{s=0}^{s=a} H(t-1) h(t) dt + (4\pi na^3) r \int_0^1 sh(s) ds,
\]

\[
h(r) = \tau(r), \tag{2}
\]

\( a \) is the diameter of the sphere.

Equation (2) is just the special case appropriate to hard spheres of a general relation due to Broyles.5 From the definitions of \( h(r) \) and \( \tau(r) \) one has for hard
spheres,

\[ g(r) = \begin{cases} 0 & r < 1, \\ \frac{h(r)}{r} & r > 1. \end{cases} \] 

(3)

An examination of the derivatives of \( h(r) \) shows that there is a discontinuity in the fourth and higher derivatives of \( h(r) \) at \( r = 1 \), and a discontinuity in the second and higher derivative at \( r = 2 \). These discontinuities cause further discontinuities in the derivatives at \( r = 3, 4, \) etc. This leads us to consider the possibility of a piecewise analytic solution to Eq. (2). We define the functions \( h_n(r) \) by the relations

\[ h_0(r) = h(r) \quad 0 < r < 1, \]
\[ h_1(r) = h(r) \quad 1 < r < 2, \]
\[ h_n(r) = h(r) \quad n < r < n+1. \] 

(4)

Using these definitions and by differentiating equation (2) we obtain the following chain of equations for the \( h_n(r) \)'s.

\[ h_0'(r) = 1 - 3p \int_0^1 h_0(s) h_1(r+s) ds + 6p \int_0^1 s h_0(s) ds, \]
\[ h_1'(r) = 1 - 3p \int_0^2 h_0(s) h_1(r+s) ds \]
\[ - 3p \int_0^1 h_0(s) h_2(r+s) ds + 3p \int_0^{r-1} h_0(s) h_1(r-s) ds + 6p \int_0^1 s h_0(s) ds, \]
\[ h_n'(r) = 1 - 3p \int_0^{n+1-r} h_0(s) h_n(r+s) \]
\[ - 3p \int_0^{n+1-r} h_0(s) h_{n+1}(r+s) + 3p \int_0^{r-n} h_0(s) h_n(r-s) \]
\[ + 3p \int_0^1 h_0(s) h_{n-1}(r-s) + 6p \int_0^1 s h_0(s) ds, \quad n \geq 2. \] 

(5)

Here we have introduced the dimensionless number density

\[ \rho = \frac{3}{2} (\pi a^3 n). \]

(6)

Equations (5) can be made the basis for finding formal expressions for the terms in the familiar expansion of \( g(r) \) in powers of \( \rho \). If we let

\[ h_n(r) = \sum_{j=0}^{\infty} W_{n,j}(r) \rho^j, \]

(7)

then one finds \( W_{n,0}(r) = r^n \) for all \( n \). The \( W_{n,j}(r) \) terms for a higher \( j \) will be given in terms of integrals of the same form as the integrals in Eq. (5), with integrands containing products of \( W_{n,j-1}, W_{n,j-2}, \) etc. Hence all the \( W_{n,j}(r) \) terms will be analytic in the interval \( n \) to \( n+1 \). If the power series (7) converges absolutely for some finite radius of convergence in \( \rho \), then the functions \( h_n(r) \) will be analytic in the interval \( n < r < n+1 \). We shall therefore look for a piecewise analytic solution for \( h(r) \) with discontinuities at \( r = 1, 2, 3 \ldots \).

 Upon returning to Eq. (2), and taking the Laplace transform of both sides we obtain

\[ \int_0^\infty h(r) \exp(-\lambda r) dr = a \int_0^\infty \rho \exp(-\lambda r) d\rho \]
\[ - 3p \int_0^\infty \exp(-\lambda r) \int_0^1 h_0(s) \int_{t-1}^{t+\lambda} H(t-1) h(t) dt, \]
\[ a = 1 + 6p \int_0^1 s h_0(s) ds. \] 

(8)

By interchanging the order of integration, one finds

\[ \int_0^\infty \exp(-\lambda r) \int_0^1 h_0(s) ds \int_{t-1}^{t+\lambda} H(t-1) h(t) dt \]
\[ = \int_0^1 h_0(s) ds \int_0^\infty h(t) dt \int_{t-1}^{t+\lambda} \exp(-\lambda r) dr. \] 

(9)
Upon doing the \( r \) integration in (9), and substituting in (8) one finds, after some elementary manipulation,

\[
\int_1^\infty h(r) \exp(-\lambda r) dr = \left\{ \frac{a}{\lambda^2} - \int_1^1 \exp(-\lambda s) h_0(s) ds \right\} \left( 1 + 3\rho \int_1^1 \exp(\lambda s) h_0(s) ds - 3\rho \int_1^1 \exp(-\lambda s) h_0(s) ds \right).
\] (10)

We shall now determine a set of sufficient conditions on \( h_0(s) \) in order that \( h(r) \) as defined by the inverse Laplace transform of the rhs of (10) be piecewise analytic in the manner described.

By Definition (4) we have

\[
\int_1^\infty h(r) \exp(-\lambda r) dr = \sum_{n=1}^\infty \int_n^{n+1} h_n(s) \exp(-\lambda s) ds.
\] (11)

We also note the following identities which can be proved by repeated integration by parts:

\[
\int_n^{n+1} h_n(s) \exp(-\lambda s) ds = \exp(-n\lambda) \sum_{l=0}^{n} \left[ h_n^{(l)}(n)/\lambda^{l+1} \right]
\]

\[
\int_1^1 \exp(-\lambda s) h_0(s) ds = - \exp\left[ -(n+1)\lambda \right] \sum_{l=0}^{n} \left[ h_n^{(l)}(n+1)/\lambda^{l+1} \right]
\]

\[
\int_1^1 \exp(\lambda s) h_0(s) ds = \exp\left[ (n+1)\lambda \right] \sum_{l=0}^{n} \left[ h_n^{(l)}(1)/\lambda^{l+1} \right]
\]

\[
\int_1^1 \exp(-\lambda s) h_0(s) ds = - \exp\left[ -(n+1)\lambda \right] \sum_{l=0}^{n} \left[ h_n^{(l)}(1)/\lambda^{l+1} \right]
\]

\[
\int_1^1 \exp(\lambda s) h_0(s) ds = \exp\left[ (n+1)\lambda \right] \sum_{l=0}^{n} \left[ h_n^{(l)}(0)/\lambda^{l+1} \right]
\]

\[
\int_1^1 \exp(-\lambda s) h_0(s) ds = - \exp\left[ -(n+1)\lambda \right] \sum_{l=0}^{n} \left[ h_n^{(l)}(0)/\lambda^{l+1} \right].
\] (12)

Here the superscript \( l \) denotes the \( l \)th derivative. From (10), (11), (12)

\[
\exp(-\lambda) \sum_{l=0}^{n} \left[ h_n^{(l)}(1)/\lambda^{l+1} \right]
\]

\[
+ \sum_{n=2}^{\infty} \exp(-n\lambda) \sum_{l=0}^{n} \left[ h_n^{(l)}(n) - h_{n-1}^{(l)}(n) \right]
\]

\[
= \frac{\exp(-\alpha \beta - \epsilon)}{\gamma e^{-\alpha \lambda} + \delta e^{-\lambda} + \epsilon}.
\]

\[
\alpha = (a/\lambda^2) - \sum_{l=0}^{\infty} \left[ h_0^{(l)}(0)/\lambda^{l+1} \right],
\]

\[
\beta = \sum_{l=0}^{\infty} \left[ h_0^{(l)}(1)/\lambda^{l+1} \right],
\]

\[
\gamma = (3p/\lambda) \sum_{l=0}^{\infty} \left[ h_0^{(l)}(1)/\lambda^{l+1} \right],
\]

\[
\delta = 1 - (6p/\lambda) \sum_{l=0}^{\infty} \left[ h_0^{(l)}(0)/\lambda^{l+1} \right],
\]

\[
\epsilon = (3p/\lambda) \sum_{l=0}^{\infty} \left[ (-1)^l h_0^{(l)}(1)/\lambda^{l+1} \right].
\]

Consider for the moment the expansion of the rhs of (13) in powers of \( e^{-\lambda} \). The first term in this expansion is

\[
\frac{\alpha}{e^{-\lambda}} = \left\{ \frac{a}{\lambda^2} \sum_{l=0}^{\infty} \left[ h_0^{(l)}(0)/\lambda^{l+1} \right] \right\} / \frac{3p}{\lambda} \sum_{l=0}^{\infty} \left[ (-1)^l h_0^{(l)}(1)/\lambda^{l+1} \right] e^{-\lambda}.
\] (14)

The denominator in this expression is of the form

\[
(3p/\lambda^2) h_0^{(1)}(1) + O(1/\lambda^2).
\]

We see from (13) that the coefficient of \( e^{-\lambda} \) must be a pure Laurent series of the form

\[
(a/\lambda) + O(1/\lambda^2).
\]

This can only be possible if the numerator in (14) is of the form

\[
(a^2/\lambda^3) + O(1/\lambda^4),
\]

which implies the following two relationships

\[
h_0^{(1)}(0) = 0,
\]

\[
h_0^{(1)}(0) = a.
\] (15)

The relations (15) could be obtained immediately as necessary conditions on \( h_0(r) \) by setting \( r = 0 \) in the expressions for \( h_0(r) \) and \( h_0'(r) \).

In general the coefficient for the term \( e^{-\lambda} \) in the rhs of (13) will contain a denominator \( \exp(-\alpha \lambda) \) which will then be of the form

\[
[(3p/\lambda^2) h_0^{(1)}(1) + O(1/\lambda^3)],
\]

which will impose \( 2n \) relations connecting the values of the derivatives of \( h_0(r) \) evaluated at \( r = 0 \) and \( r = 1 \).

We will now show that if, in the expression on the rhs of (13), \( \alpha + \beta e^{-\lambda} \) is a factor of \( \gamma e^{-\lambda} + \delta e^{-\lambda} + \epsilon \), then all of these relations for any \( n \) are automatically satisfied. The factoring relation

\[
(\alpha + \beta e^{-\lambda}) \left\{ (\gamma x/\beta) + \left[ (\delta \beta - \alpha \gamma)/\beta^2 \right] \right\} = \gamma x^2 + \delta x + \epsilon
\] (16)

implies that

\[
\alpha \left[ \delta - (\alpha \gamma/\beta) \right] = \epsilon \beta.
\] (17)
One then obtains from (17) using the Definitions (13)

\[
\left[ \frac{a}{x^2} - \sum_{j=0}^\infty \frac{h_0'(0)}{\lambda^{j+1}} \right] e^\lambda \left\{ \left[ 1 - \frac{3p \sum_{j=0}^{l(\text{even})} \frac{h_0'(0)}{\lambda^{j+1}}} \right] \right\} = \frac{3p \sum_{j=0}^{l(\text{even})} (-1)^j h_0'(1)^j}{\lambda^{j+1}}.
\]

(18)

We have simplified Expression (18) by using Relations (15), along with the fact that \( h_0(r) - ar \) is an even function. If Condition (18) is met then the rhs of (13) becomes

\[
e^\lambda \left[ \sum_{j=0}^{l(\text{even})} \frac{h_0'(1)^j}{\lambda^{j+1}} \right] \left[ 1 - \frac{3p \sum_{j=0}^{l(\text{even})} \frac{h_0'(0)}{\lambda^{j+1}}} \right] \left[ 1 + \frac{3p \sum_{j=0}^{l(\text{even})} \frac{h_0'(1)^j}{\lambda^{j+1}}} e^\lambda \right] \left[ 1 - \frac{3p \sum_{j=0}^{l(\text{even})} \frac{h_0'(0)}{\lambda^{j+1}}} \right]^{-1}.
\]

Clearly, the coefficient of \( \exp(-n\lambda) \) in the expansion of this expression will have a pure Laurent series expansion in \( \lambda \). It is then easy to show that this is a sufficient condition that the inverse Laplace transform exists, and is piecewise analytic in the manner described.

We now examine the conditions (18) more closely. After some manipulation (18) becomes

\[
-\sum_{j=0}^{l(\text{even})} \frac{h_0'(0)}{\lambda^{j+1}} + \frac{a}{x^2} = -\frac{3p \sum_{j=0}^{l(\text{even})} \frac{1}{\lambda^{j+2}} \sum_{j=2}^{l(\text{even})} h_0'(0)^j h_0^{n-j}(0) + \frac{3p \sum_{j=0}^{l(\text{even})} \frac{1}{\lambda^{j+2}} \sum_{j=0}^{l(\text{even})} (-1)^j h_0'(1)^j h_0^{n-j}(1)}{1 - \frac{3p \sum_{j=0}^{l(\text{even})} \frac{h_0'(0)}{\lambda^{j+1}}} e^\lambda}.
\]

(19)

Equating powers in \( 1/\lambda \), one finds

\[
\begin{align*}
h_0'(0) &= 0, \\
h_0'(0) &= a, \\
-h_0'(0) &= 3ph_0'(1)h_0'(1), \\
h_0'(0) &= 0, \\
-h_0'(0) &= 3p[2h_0'(1)h_0'(1) - h_0'(1)h_0'(1)], \\
h_0'(0) &= 0, \\
-h_0'(0) &= 3p \sum_{j=0}^{n(\text{odd})} (-1)^j h_0'(1)^j h_0^{n-j}(1) \\
-h_0'(0) &= 3p \sum_{j=0}^{n(\text{even})} (-1)^j h_0'(1)^j h_0^{n-j}(1) \\
-h_0'(0) &= 3p \sum_{j=0}^{n(\text{even})} (-1)^j h_0'(0)^j h_0^{n-j}(0) + \frac{3p \sum_{j=0}^{l(\text{even})} \frac{1}{\lambda^{j+2}} \sum_{j=0}^{l(\text{even})} (-1)^j h_0'(1)^j h_0^{n-j}(1)}{1 - \frac{3p \sum_{j=0}^{l(\text{even})} \frac{h_0'(0)}{\lambda^{j+1}}} e^\lambda}.
\end{align*}
\]

(20), (21), (22)

Where the last equality in (22) follows from the identity

\[
2 \int_0^1 h_0^{n-1}(s) h_0(s) ds = \sum_{k=0}^{n-2} (-1)^k h_0'(1)^k h_0^{n-5}(1)
\]

and Relations (21). The first 10 of Relations (20), (21), and (22) can be derived as necessary conditions on \( h_0(r) \) by an examination of the values of \( h_0(r) \), \( h_1(r) \) \( \cdots \) \( h_9(r) \) and some of the derivatives of these functions at the points \( r=0, 1, 2 \cdots 5 \). The process can no doubt be continued but becomes more and more lengthy, requiring relations at points further from the origin as the order of the derivative of \( h_0(r) \) is increased.

In summary we have derived all the relations as sufficient conditions for the function \( h_0(r) \), and have good reason to suspect that they're all also necessary conditions.

It is clear from the Eqs. (21) and (22) that an \( h_0(r) \) of the form

\[
h_0(r) = ar + br^2 + cr^4
\]

(23)

satisfies Eqs. (21) and (22) identically. The following argument suggests very strongly that \( h_0(r) \) must be of this form. Suppose that we try to satisfy the relations (20), (21), (22) with a polynomial

\[
h_0(r) = ar + br^2 + cr^4 + \cdots + \gamma r^n
\]

\( n \geq 6 \)

where \( n \) is any even finite integer. Then the relation for \( h_0^n(0) \) reads

\[
-h_0^n(0) = 6p \int_0^1 h_0^{n-1}(s) h_0(s) ds = 6p h_0^n(0) \int_0^1 s h_0(s) ds.
\]

(22)

Hence, either

\[
h_0^n(0) = n! \omega = 0,
\]

or

\[
a = 1 + 6p \int_0^1 s h_0(s) ds = 0.
\]

\( a \) cannot be identically zero since this leads to the physically impossible result that the compressibility is infinite at all densities [see Eq. (31)]. The second alternative is therefore impossible except at an isolated number of values of \( \rho \), since \( a \) is an analytic function of \( \rho \).

Therefore, if one tried to fit the first \( n \) relations (20), (21), (22) with any polynomial of finite order, one would be forced back to the form given in Eq. (23).
Substituting (23) in (20) gives the following relations for \( a, b, \) and \( c \):

\[
a = 1 + 6p(\frac{3a + 1}{3} + \frac{1}{3}c),
\]

\[
2b = -3p(a + b + c)^2,
\]

\[
24c = -3p[2(a + b + c)(2b + 12c) - (a + 2b + 4c)^2].
\]

The solution to these equations is

\[
a = \frac{(2x+1)^2}{(x-1)^4},
\]

\[
b = -\frac{(12x + 12x^2 + 3x^3)}{2(x-1)^4},
\]

\[
c = \frac{x(2x+1)^2}{2(x-1)^4},
\]

\[x = \frac{1}{4}p.\]  

(24)

The function \( h_0(r) \) is then completely determined via equations (23) and (24).

**EQUATIONS OF STATE**

There are two familiar methods of calculating the equation of state when the radial distribution function is known. The first uses the relation

\[
P = nkT - \frac{n^2}{6} \int r \phi'(r) g(r) \, dr,
\]

which was originally derived from the virial theorem.\(^6\)

The second uses the Ornstein-Zernike relation,\(^6\)

\[
kT \frac{\partial m}{\partial P} = 1 + m \int (g(r) - 1) \, dr.
\]

Following Rushbrooke\(^6\) we refer to (25) as the pressure equation and (26) as the compressibility equation. For an exact \( g(r) \) these two relations must give the same equation of state. This does not hold for an approximate \( g(r) \), and the magnitude of the difference between the two results is in this sense an indication of the size of the error in \( g(r) \).

For hard spheres, Relation (25) reduces to

\[
P \rho^3(\pi a^3) = kT[\rho + \rho^2 g(1)].
\]

(27)

Here we use the dimensionless number density defined in Eq. (6). Relation (26) becomes

\[
\frac{kT \phi}{\partial (2\pi a^3/3) P} = 1 + 6p \left[ \int_1^\infty (g(r) - 1) r^2 \, dr - \frac{1}{3} \right].
\]

(28)

Since \( g(1) = h(1) = h_0(1) \) the evaluation of (27) is immediately obvious. It is also possible to evaluate the rhs of (28) in terms of \( h_0(r) \). From the definition of \( h(r) \),

\[
\int_1^\infty r^2 [g(r) - 1] \, dr = \int_1^\infty s h_0(s) \, ds.
\]

(29)

Multiplying the Percus-Yevick equation [Eq. (2)] by \( r \) and integrating over \( r \) first, as in the Laplace transform derivation, one obtains

\[
\int_1^\infty r^2 [h(r) - r] \, dr = \left[ \int_0^1 s h_0(s) \, ds \right] + \frac{1}{3}.
\]

(30)

From (28), (29), and (30)

\[
\frac{kT \phi}{\partial (2\pi a^3/3) P} = \left[ 1 + 6p \int_0^1 s h_0(s) \, ds \right]^{-1}.
\]

(31)

One can now use the results of the last section for \( h_0(r) \), Eqs. (23) and (24), to obtain

\[
P = nkT[1 + 2x + 3x^2]/(1 - x)^4] \quad \text{pressure equation}
\]

(32)

and

\[
P = nkT[(1 + x + x^2)/(1 - x)^4] \quad \text{compressibility equation}
\]

(33)

We note that the only singularity in the expressions for \( P \) is a pole at \( x = 1 \), or \( \rho = 4 \). The density \( \rho = 4 \) corresponds to the physically impossible density at which all space is filled. The closest-packed density is \( \rho = \frac{4}{3}(\pi \sqrt{2}) \). We see therefore that the Percus–Yevick equation predicts no phase transition, and must fail at densities near the density of closest packing. The compressibility equation is identical with one derived by Reiss, Frisch and Lebowitz.\(^7\)

In Fig. 1 we compare the Percus–Yevick equations

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of state with the dynamical equations results of Wainwright and Alder. The results of Wainwright and Alder in excellent agreement with the Monte Carlo results of Wood, Parker, and Jacobson. From Fig. 1 we see that the Percus–Yevick equations of state bracket Wainwright and Alder’s results for the fluid branch. The compressibility equation gives somewhat better results than the pressure equation in accord with the suggestion by Percus and Yevick. The Born, Green, Yvon result is also plotted in Fig. 1 for comparison.

CONCLUSION

In this paper we have calculated exact expressions for both the compressibility and pressure equations of state predicted by the Percus–Yevick equation for hard spheres. The good agreement found between these results and the “exact” machine calculations helps confirm the superiority of the Percus–Yevick equation, as noted in some previous comparisons.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge my indebtedness to Dr. Marshall Fixman and Dr. G. S. Rushbrooke for many helpful discussions and suggestions concerning this problem.

Resolution of Exact $H_2^+$ Wavefunction on One-Center Hydrogenic Basis

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(Received 19 February 1963)

The ground state of $H_2^+$ is treated by a variational procedure, using as basis functions discrete hydrogen-like orbitals located at the midpoint. The variational coefficient for each function is compared to its overlap with the exact function. The effect of using different $Z$'s for the basis sets is studied. When the basis set is not well chosen, the variational coefficients may differ radically from the values determined by the overlaps. The nodal properties of the basis functions, rather than their energies, are emphasized.

A COMMON form of trial function used in variational calculations in a molecular problem is a linear combination of fixed basis functions, say the set $\{\phi_i\}$, with variable coefficients

$$\psi = \sum_{i=1}^{n} c_i \phi_i.$$  

(1)

The variation of the coefficients $c_i$ to minimize the energy leads to the secular equation, i.e., the relative contribution of a basis function is determined by the values of the matrix elements of the Hamiltonian. If the exact wavefunction is known, it may be resolved quite simply, and without reference to energy, onto the functions of a complete basis set. Let the expansion of the exact wavefunction $\Psi$ in the complete set $\{\psi_i\}$ be written as

$$\sum_{i=1}^{m} A_i \psi_i.$$  

Then, if the $\{\psi_i\}$ are orthonormal, the coefficient $A_i$ is given by

$$A_i = \int \psi_i^* \Psi \, dr \bigg/ \left( \int \Psi^* \Psi \, dr \right)^{1/2},$$

(2)

which expression emphasizes the importance of overlap and hence nodal properties.

It is well known that, if the relative error in the energy calculated with an approximate wave function is of size $\epsilon^2 (\epsilon < 1)$, then the root-mean-square deviation of this wavefunction from the true wavefunction is of size $\epsilon$. The size of $\epsilon$ will be reflected in the errors in the expectation values of various operators. The variationally determined coefficients themselves, the $c_i$, are often given significance (population analysis), although they have no physical meaning. They may or may not resemble the true expansion coefficients, whether or