

Correlation coefficient and electron correlation

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The correlation coefficient which is used in mathematical statistics is evaluated for an exactly soluble electron correlation problem. Our results show that a wave function with a very "negative" correlation coefficient is not necessarily energetically (hence variationally) a good approximation to the exact wave function. We discuss the importance of this result *vis-a-vis* the notion in the literature that the correlation coefficient provides a useful tool for analyzing approximate wave functions.

I. INTRODUCTION

The correlation coefficient for two variables (say \mathbf{r}_1 and \mathbf{r}_2) is defined as

$$\rho[\mathbf{r}_1, \mathbf{r}_2] \equiv \frac{\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle - \langle \mathbf{r}_1 \rangle \cdot \langle \mathbf{r}_2 \rangle}{\prod_{k=1}^2 (\langle r_k^2 \rangle - \langle \mathbf{r}_k \rangle \cdot \langle \mathbf{r}_k \rangle)^{1/2}} \quad (1)$$

An important result from the theory of statistics is that $|\rho| \leq 1$. The lower limit corresponds to perfect negative correlation (i.e., $\mathbf{r}_1 = -\mathbf{r}_2$), and the result $\rho = 0$ means either \mathbf{r}_1 is independent of \mathbf{r}_2 or that they are correlated in a particular way (say, $\mathbf{r}_1 \perp \mathbf{r}_2$).

Kutzelnigg, Del Re, and Berthier,¹ as well as Banyard²⁻⁴ suggested the use of the correlation coefficient as a measure of electron correlation in wave functions which go beyond the Hartree-Fock level of approximation. It is, however, to be noted that "independent" particle models (e.g., Hartree-Fock theory) do not necessarily imply $\rho = 0$; that is, the particles are not independent in the sense employed in mathematical statistics.

Owing to the difficulty of evaluating the necessary integrals using reasonably well-correlated wave functions, Kutzelnigg *et al.* restricted their numerical evaluations to two special cases; a radial correlation coefficient [involving r_1^{-1} and $(r_1 r_2)^{-1}$] and an angular correlation coefficient ($\langle \mathbf{r}_1 \rangle = \langle \mathbf{r}_2 \rangle = 0$). Among their conclusions, Kutzelnigg *et al.* point out that in these simple special cases for ground states of atoms the correlation coefficients are very small, as if the electrons were more or less independent.

In the following section we consider a model two electron problem where the Hamiltonian includes an electron interaction term. The problem is solved exactly, and the correlation coefficient ρ [Eq. (1)] is evaluated for the exact wave function. Although ρ is negative it may be close to zero, depending on the parametrization of our model Hamiltonian. Furthermore, energetically crude

approximations to the exact wave function are shown to give ρ close to -1 . Thus, a wave function with a very "negative" correlation coefficient is not necessarily energetically (hence variationally) a good approximation to the exact wave function. Although the correlation coefficient provides a measure of electron "correlation" in the probabilistic sense of the term, it does not necessarily measure electron correlation in the energetic sense of the term. In view of this, it appears most sensible to restrict the analysis of electron correlation via various correlation coefficients to very accurate wave functions.

II. THEORY

Davidson⁵ reported an exactly soluble problem of two interacting electrons trapped in an external harmonic oscillator potential. The Hamiltonian for the problem is

$$\mathcal{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}k(r_1^2 + r_2^2) - \frac{1}{2}\alpha r_{12}^2 \quad (2)$$

Upon introducing the variables

$$\mathbf{R} = 2^{-1/2}(\mathbf{r}_1 + \mathbf{r}_2), \quad (3)$$

$$\mathbf{r} = 2^{-1/2}(\mathbf{r}_1 - \mathbf{r}_2), \quad (4)$$

the exact solution to the Schrödinger equation is obtained; for the ground state

$$\Psi^{(0)} = \psi(\mathbf{R})\phi(\mathbf{r})[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/2^{1/2}, \quad (5)$$

$$\psi(\mathbf{R}) = (k^{1/2}/\pi)^{3/4} \exp(-\frac{1}{2}k^{1/2}R^2), \quad (6)$$

$$\phi(\mathbf{r}) = (k_\alpha^{1/2}/\pi)^{3/4} \exp(-\frac{1}{2}k_\alpha^{1/2}r^2), \quad (7)$$

where

$$k_\alpha \equiv (k - 2\alpha). \quad (8)$$

The exact ground-state energy is given by

$$E^{(0)} = \frac{3}{2}(k^{1/2} + k_\alpha^{1/2}). \quad (9)$$

Evaluation of the correlation coefficient ρ is facilitated by the formula (see Feller⁶)

$$\text{var}(\mathbf{r}_1^* \pm \mathbf{r}_2^*) = 2\{1 \pm \rho[\mathbf{r}_1, \mathbf{r}_2]\}, \quad (10)$$

where

$$\bar{\mathbf{r}}_k^* \equiv (\bar{\mathbf{r}}_k - \langle \bar{\mathbf{r}}_k \rangle) / [\text{var}(\bar{\mathbf{r}}_k)]^{1/2}. \quad (11)$$

(As the variance is never negative, it is clear from (10) that $|\rho|$ does not exceed unity.) Now,

$$\text{var}(\bar{\mathbf{r}}_1^* + \bar{\mathbf{r}}_2^*) = 2\langle R^2 \rangle / \langle r_1^2 \rangle, \quad (12)$$

$$\text{var}(\bar{\mathbf{r}}_1^* - \bar{\mathbf{r}}_2^*) = 2\langle r^2 \rangle / \langle r_1^2 \rangle, \quad (13)$$

and

$$\langle R^2 \rangle = 3(2k^{1/2})^{-1}, \quad (14)$$

$$\langle r^2 \rangle = 3(2k_\alpha^{1/2})^{-1}. \quad (15)$$

The Appendix shows the derivation of Eqs. (12) and (13) in some detail.

Substitution of Eqs. (12)–(15) into (10) gives the correlation coefficient for the exact solution to the Schrödinger equation

$$\rho^{(0)}[\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2] = (k_\alpha^{1/2} - k^{1/2}) / (k_\alpha^{1/2} + k^{1/2}). \quad (16)$$

Note that if $k_\alpha = k$ (i.e., $\alpha = 0$) the value of $\rho^{(0)}$ is zero. This corresponds, of course, to two independent electrons. If $k_\alpha \rightarrow 0$ (i.e., $2\alpha \rightarrow k$) we find that $\rho^{(0)} \rightarrow -1$. This corresponds to two perfectly negatively correlated electrons, a physically interesting result as in this case the two electrons repel each other to the extent that the external harmonic oscillator potential cannot bind both electrons.

Consider an approximate wave function

$$\tilde{\Psi} = \psi(\bar{\mathbf{R}}) \bar{\phi}^\beta(\bar{\mathbf{r}}), \quad (17)$$

where ψ is given by Eq. (6),

$$\bar{\phi}^\beta(\bar{\mathbf{r}}) = (\beta^{1/2}/\pi)^{3/4} \exp(-\frac{1}{2}\beta^{1/2}r^2), \quad (18)$$

and β is a variational parameter.

If the parameter α in \mathcal{H} is small, the exact correlation coefficient $\rho^{(0)}$ is a small negative number. Furthermore, with an appropriate choice of β the approximate wave function $\tilde{\Psi}$ gives a correlation coefficient $\tilde{\rho}$ which is slightly more positive than -1 . With this choice of β , $\tilde{\Psi}$ is energetically (hence variationally) a poor approximation to $\Psi^{(0)}$ ($\bar{E} \approx 3/2k^{1/2}$ versus $E^{(0)} \approx 3k^{1/2}$) despite the nearly

perfect, negative correlation coefficient.

This model problem clearly illustrates an important consideration, namely, that the correlation coefficient does not measure electron correlation in the energetic sense of the term. Although it is necessary to exercise caution in generalizing conclusions from a model problem such as the one treated herein, it is suggested that the (probabilistic) measure of electron correlation provided by the correlation coefficient is useful in the analysis of approximate wave functions only when the exact (or very accurate) wave function is already available.

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APPENDIX

As requested by a referee, details of the derivation of Eqs. (12) and (13) are presented in this Appendix.

The variance associated with a vector quantity $\bar{\mathbf{x}}$ may be defined as follows (see Feller⁶)

$$\text{var}(\bar{\mathbf{x}}) = \langle \bar{\mathbf{x}} \cdot \bar{\mathbf{x}} \rangle - \langle \bar{\mathbf{x}} \rangle \cdot \langle \bar{\mathbf{x}} \rangle. \quad (A1)$$

Because $|\psi|^2$ is symmetric in coordinates $\bar{\mathbf{r}}_1$ and $\bar{\mathbf{r}}_2$, $\text{var}(\bar{\mathbf{r}}_1) = \text{var}(\bar{\mathbf{r}}_2)$. Thus, from Eqs. (3) and (11),

$$\bar{\mathbf{r}}_1^* + \bar{\mathbf{r}}_2^* = 2^{1/2}(\bar{\mathbf{R}} - \langle \bar{\mathbf{R}} \rangle) / [\text{var}(\bar{\mathbf{r}}_1)]^{1/2}. \quad (A2)$$

Note that $\langle \bar{\mathbf{R}} \rangle$ vanishes by symmetry. Thus, from Eq. (A1),

$$\text{var}(\bar{\mathbf{r}}_1^* + \bar{\mathbf{r}}_2^*) = 2\langle \bar{\mathbf{R}} \cdot \bar{\mathbf{R}} \rangle / [\text{var}(\bar{\mathbf{r}}_1)]^{1/2}. \quad (A3)$$

Again, using Eq. (A1), we obtain

$$\text{var}(\bar{\mathbf{r}}_1) = \langle \bar{\mathbf{r}}_1 \cdot \bar{\mathbf{r}}_1 \rangle - \langle \bar{\mathbf{r}}_1 \rangle \cdot \langle \bar{\mathbf{r}}_1 \rangle. \quad (A4)$$

The second term vanishes by symmetry. Upon combining Eqs. (A3) and (A4), one obtains Eq. (12) of the text. The derivation of Eq. (13) is a trivial analog of the derivation of Eq. (12).

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