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ARTICLE

The Ornstein–Zernike equation in molecular electronic structure theory

David Case and Frederick R. Manby[†]
Centre for Computational Chemistry, School of Chemistry, Cantocks Close
University of Bristol, Bristol BS8 1TS, UK
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The Ornstein–Zernike equation expresses a simple relationship between direct and full correlation effects of a many-body system. Although it was introduced in the context of fluids, it can be derived through simple physical arguments that are equally applicable to the electrons in a molecule. Direct correlation effects account for the correlation between two particles at a time. If a simple model for direct correlation can be found, the Ornstein–Zernike equation can be used to convert it to a treatment of the full correlation effect. We show that the independent electron pair approximation (IEPA) is a reasonable model for the description of direct correlation effects. IEPA followed by our Ornstein–Zernike treatment is closer to CCSD(T) than is CCSD for valence correlation energies of small molecules.

1. Introduction

In the Bakerian lecture of 1869, which incidentally appears never to have taken place [1], Thomas Andrews reported his observations on the liquefaction of gases under high pressure [2]. He had prepared carbon dioxide at or near its critical point and when the temperature or pressure was ‘suddenly diminished’ he observed ‘flickering striæ’.

His flickering striæ were a manifestation of critical opalescence, and the phenomenon was later described by Smoluchowski [3] and Einstein [4] in terms of spontaneous density fluctuations in the fluid. In this early work ‘mutual independence of the elements of volume’ was assumed [5]: the theoretical apparatus needed to treat correlations between the density fluctuations was devised by Ornstein and Zernike [5].

Consider a simple (atomic), homogeneous fluid with density ρ . The radial distribution function $g(r)$ expresses the extent to which the density is modified by correlations; so if there is a particle at position \mathbf{r}_1 , the density at \mathbf{r}_2 will be $\rho g(|\mathbf{r}_1 - \mathbf{r}_2|) \equiv \rho g_{12}$. In the long range the correlations die out, so $g(r) \rightarrow 1$ as $r \rightarrow \infty$. It is convenient to consider the shifted quantity $h = g - 1$, called the total correlation function [6].

In the Ornstein–Zernike (OZ) equation the total correlation function is related to a new quantity c_{12} , the direct correlation function:

$$h_{12} = c_{12} + \rho \int d\mathbf{r}_3 c_{13} h_{32} . \tag{1}$$

The equation expresses the idea that the total correlation between particles arises

[†]Corresponding author: fred.manby@bris.ac.uk

1 primarily from the direct correlation effect, but with a correction arising from
 2 higher-order effects that bring in more and more additional particles. This leads
 3 to the interpretation of direct correlation as the correlation effect between just two
 4 particles in a homogenous background density.
 5

6 With this in mind, the OZ equation can be ‘derived’ based on the following
 7 physical arguments.

- 8 (1) Assume there is a particle at position \mathbf{r}_1
- 9 (2) The direct correlation effect modifies the density at \mathbf{r}_2 by an amount ρc_{12}
- 10 (3) The density at \mathbf{r}_3 is modified as well, by the amount ρc_{13}
- 11 (4) *This* fluctuation at \mathbf{r}_3 has an additional effect on the density at \mathbf{r}_2 , with
 12 magnitude $\rho c_{13} \rho c_{32}$
- 13 (5) Particle 3 can be anywhere, and after integrating over \mathbf{r}_3 and cancelling
 14 one power of ρ , one obtains

$$15 \quad h_{12} \approx c_{12} + \rho \int d\mathbf{r}_3 c_{13} c_{32}$$

- 16
- 17
- 18
- 19
- 20
- 21 (6) The entire argument can be repeated with more intermediate particles,
 22 giving the infinite series

$$23 \quad h_{12} = c_{12} + \rho \int d\mathbf{r}_3 c_{13} c_{32} + \rho^2 \int d\mathbf{r}_3 c_{13} \int d\mathbf{r}_4 c_{34} c_{42} + \dots$$

- 24
- 25
- 26
- 27 (7) And finally, this series can be summed by a simple substitution to give the
 28 OZ equation.

29
 30 The Ornstein–Zernike equation can be viewed as nothing more than a definition
 31 of c_{12} in terms of h_{12} . But if it turns out to be simpler to make approximate
 32 descriptions of the direct correlation function, the OZ equation can be used to
 33 convert c_{12} to the full correlation function, h_{12} . In the context of simple liquids it
 34 was found that the structure of c_{12} was much simpler than that of h_{12} . The full
 35 correlation function has characteristic long-range wiggles for a fluid close to its
 36 critical point, but the direct correlation function has a simple, short-range form at
 37 all T, P [6].
 38

39 Nothing in the physical argument above is special to simple fluids. In fact the
 40 OZ equation can just as well be applied to the electrons in a molecule. In elec-
 41 tronic structure theory the familiar objects are two-particle densities (rather than
 42 correlation functions) and the system of interest is non-uniform. This suggests a
 43 recasting of the OZ equation in the form
 44

$$45 \quad \rho_{12}^h = \rho_{12}^c + \int d\mathbf{r}_3 \frac{1}{\rho(\mathbf{r}_3)} \rho_{13}^c \rho_{32}^h \quad (2)$$

46
 47
 48 which is achieved by introducing spatial dependence in the one-particle densities
 49 and substituting the definitions $\rho_{12}^h = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h_{12}$ and $\rho_{12}^c = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)c_{12}$ into
 50 Equation (1).
 51

52 In Equation (2) the two-particle densities have the following interpretation: ρ_{12}^h
 53 is the correlation component of the exact reduced two-particle density; and ρ_{12}^c is
 54 the correlation component from a calculation that only includes the effects of direct
 55 correlation. If a simple model for ρ_{12}^c can be found, Equation (2) can be used to
 56 convert it into the total correlation component of the two-particle density.
 57

58 The physically motivated ‘derivation’ above is quite compelling, but in any case
 59 there are various connections to more formal theory. The OZ equation emerges quite
 60

naturally in density functional theory (DFT) of fluids [7] or indeed of electrons. In fluids the direct correlation function is defined as a second functional derivative of the excess energy functional (that is the total energy minus the ideal or non-interacting contribution) [7]:

$$c_{12}^{\text{fluid}} = -\frac{\delta^2 \beta(\mathcal{F}[\rho] - \mathcal{F}_{\text{id}}[\rho])}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}. \quad (3)$$

The quantum analogue of the OZ equation has been investigated by Chihara in the context of ionic liquids [8] and liquid metals [9]. In zero-temperature electronic density functional theory an Ornstein–Zernike equation can still be derived, but in this case the h_{12} is related to a density response function, not a 2-particle density, and the c_{12} is proportional to $r_{12}^{-1} + f_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2)$. This is a potentially interesting connection, since this c_{12} appears in the Dyson equation that connects the non-interacting response χ_0 to the full response χ . It is the quantity approximated by r_{12}^{-1} in the adiabatic-connection fluctuation-dissipation formulations of the random phase approximation [10]. However this connection will not be further pursued here. Instead we focus on the possible role of the OZ equation as an efficient means to build in inter-pair correlations to simple pair-based descriptions of molecular electronic structure theory.

2. The OZ equation in electronic structure theory

2.1. MP2 and direct correlation

The direct correlation function describes correlations in the system between just two particles, with the others remaining in their mean-field distribution. It should be possible to approximate the direct correlation function using what in electronic structure theory would be called a pair theory.

The simplest pair theory is MP2, and this choice also has the advantage that, to first order, the correlation contribution to the pair density is simply provided by the amplitudes:

$$\rho_{12}^{\text{MP2}} = T_{ia,jb} \psi_i^*(\mathbf{r}_1) \psi_a(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \psi_b(\mathbf{r}_2). \quad (4)$$

Moreover, the correlation energy is in turn simple to extract from this pair density:

$$E_{\text{MP2}}^{\text{corr}} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho_{12}^{\text{MP2}}}{r_{12}} \equiv \text{tr } \mathbf{TK}. \quad (5)$$

(Here we assume that the amplitudes are properly antisymmetrized and the exchange integrals are not: $K_{ia,jb} = (ia|jb)$).

The OZ equation in the basis of ia -pairs can be **found by inserting the definition in Equation (4) into Equation (1), multiplying by $\psi_i^*(\mathbf{r}_1) \psi_a(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \psi_b(\mathbf{r}_2)$, integrating over the coordinates of both electrons, and cancelling the overlap matrices that appear on the left and right of each term in the equation. This gives**

$$T_{ia,jb}^h = T_{ia,jb}^c + T_{ia,kc}^c X_{kc,\ell d} T_{\ell d,jb}^h, \quad (6)$$

4

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1 where

$$X_{kc,\ell d} = \int \frac{d\mathbf{r}}{\rho(\mathbf{r})} \psi_k(\mathbf{r})\psi_c(\mathbf{r})\psi_\ell(\mathbf{r})\psi_d(\mathbf{r}) . \quad (7)$$

2
3
4
5
6
7 **It should be noted that the derivation relies on the inversion of the**
8 **overlap matrix**

$$S_{ia,jb} = \int d\mathbf{r} \psi_i(\mathbf{r})\psi_a(\mathbf{r})\psi_j(\mathbf{r})\psi_b(\mathbf{r}) \quad (8)$$

9
10
11
12
13 **which becomes ill-conditioned in the basis-set limit; this issue has been**
14 **ignored in the present work, and in the triple-zeta basis sets used**
15 **here, the overlap matrix is invertible in double precision. A further as-**
16 **sumpinot is that it is acceptable to use the uncorrelated (Hartree–Fock)**
17 **density in the definition of X.**

18
19 It is perfectly possible to proceed directly with this equation, but the imple-
20 mentation can be made much more efficient using density fitting. Orbital pairs are
21 defined in the usual way

$$|ia\rangle = D_\mu^{ia}|\mu\rangle, \quad (9)$$

22
23
24
25 with $|\mu\rangle \equiv \Xi_\mu$ a set of atom-centered fitting functions (we use the MP2FIT sets
26 of Weigend *et al.* [11]). If density fitted MP2 is used, the exchange integrals are
27 expressed as

$$K_{ia,jb} = D_\mu^{ia} \tilde{K}_{\mu\nu} D_\nu^{jb}, \quad (10)$$

28
29
30
31
32 where $\tilde{K}_{\mu\nu} = (\mu|\nu)$, and the trace in Equation (5) can be written

$$E_{\text{MP2}}^{\text{corr}} = T_{ia,jb} D_\mu^{ia} \tilde{K}_{\mu\nu} D_\nu^{jb}. \quad (11)$$

33
34
35
36 From this equation it is obvious that the amplitudes can be projected into the
37 auxiliary basis set

$$\tilde{T}_{\mu\nu} = T_{ia,jb} D_\mu^{ia} D_\nu^{jb}. \quad (12)$$

38
39
40
41
42 Then the correlation energy can equally well be computed in the auxiliary basis as

$$E_{\text{MP2}}^{\text{corr}} = \text{tr} \tilde{\mathbf{T}} \tilde{\mathbf{K}}. \quad (13)$$

43
44
45
46
47 The OZ equation can also be written in the fitting set,

$$\tilde{\mathbf{T}}^h = \tilde{\mathbf{T}}^h + \tilde{\mathbf{T}}^c \tilde{\mathbf{X}} \tilde{\mathbf{T}}^h \quad (14)$$

48
49
50
51
52 where

$$\tilde{X}_{\mu\nu} = \int \frac{d\mathbf{r}}{\rho(\mathbf{r})} \Xi_\mu(\mathbf{r})\Xi_\nu(\mathbf{r}). \quad (15)$$

53
54
55
56
57 The X integrals (in either representation) are computed by numerical quadrature
58 on DFT integration grids. We have checked that neither grid tolerances nor the
59
60

1 threshold used to avoid divergences in $1/\rho$ have any effect on the conclusions pre-
2 sented.

3 Since both Equations (6) or (14) are formally equivalent we will now drop the
4 tildes and consider the fitted and conventional versions together. The OZ equation
5 can be simply rearranged for \mathbf{T}^h :
6

$$7 \quad \mathbf{T}^h = \mathbf{T}^c(1 - \mathbf{T}^c\mathbf{X})^{-1} \quad (16)$$

8 and a new correlation energy can be extracted as $E^h = \text{tr} \mathbf{T}^h \mathbf{K}$. For the small
9 first-row molecules we used MP2 to obtain \mathbf{T}^c , computed \mathbf{T}^h by Equation (16),
10 and then evaluated the correlation energy E^h : the results are terrible.

11 This, on proper reflection, is not altogether surprising. MP2 theory was selected
12 as a candidate for producing the direct correlation density ρ_{12}^c on the grounds of
13 being the simplest pair theory. But MP2 really is an exceptional theory, and its
14 surprising accuracy arises from partial cancellation of two rather drastic approxi-
15 mations.
16

17 First, it is an independent-pair theory. In such theories the two electrons in a
18 given pair can avoid each other without ‘worrying’ about the fact that there are
19 other electrons around. This leads to an over-estimation of correlation effects. The
20 exact independent electron pair theory, IEPA [12, 13], overestimates the correlation
21 energy by around 15% (see below), implying that the lack of treatment of inter-pair
22 correlations raises the MP2 correlation energy by a comparable amount.
23

24 But in MP2 theory the virtual Hartree-Fock eigenvalues that appear in the en-
25 ergy denominator contain a spurious Coulomb and exchange interaction with all
26 N (instead of $N - 1$) electrons [14]. This results in a spurious elevation of the
27 virtuals, an increase in the energy denominators, and, hence, an under-estimation
28 of correlation effects [15]. The spurious interactions present in the Møller-Plesset
29 denominator are explicitly subtracted in Epstein-Nesbet (EN) perturbation the-
30 ory [13, 16–18]. EN2 performs very well for systems of two (correlated) electrons
31 such as H_2 or LiH [15]. But for systems with more than two electrons (i.e. for
32 systems where inter-pair correlations become relevant) EN2 overestimates the full
33 configuration-interaction correlation energy by 15–20% [15, 18].
34

35 Thus MP2 typically gives good correlation energies as a direct result of the
36 cancellation of errors caused by neglecting inter-pair correlations and by using
37 one-particle energies with spurious interactions.
38

39 2.2. IEPA and direct correlation

40 It should be clear from the previous section that a reasonable pair theory to use as
41 a model for direct correlation is IEPA, that is, the pair theory in which the electron
42 correlation within each pair is treated exactly.
43

44 To review the argument: direct correlation, as it appears in the physical motiva-
45 tion leading to Equation (1), is the correlation between pairs of electrons, and the
46 OZ equation offers a way to introduce all of the inter-pair couplings. Therefore it
47 seems reasonable to test the ansatz $\rho_{12}^c = \rho_{12}^{\text{IEPA}}$. There are two barriers to doing
48 this directly, one technical and one theoretical. Technically it is non-trivial to ob-
49 tain the 2-particle density in IEPA, although it certainly possible and we do intend
50 to investigate this in the future. The theoretical problem is that even if one could
51 obtain the exact 2-particle density, the correlation energy only depends on the part
52 of it linear in the amplitudes, and it is not straightforward to extract this part from
53 the whole 2-particle density. Here we propose to test the ansatz of Equation (6)
54 with the definition $\mathbf{T}^c = \mathbf{T}^{\text{IEPA}}$.
55
56
57
58
59
60

2.3. Correction for finite number of particles

For infinite systems it is reasonable for the entire density ρ to appear in the integral of Equation (1). For a finite system it becomes important to resolve the fact that the density in the integral should be the total density *minus* the density distribution of the two electrons under consideration. In the present case, with the ansatz $\mathbf{T}^c = \mathbf{T}^{\text{IEPA}}$, we are in a position to identify the densities that should be subtracted, and this suggests a modification of Equation (6)

$$T_{ia,jb}^h = T_{ia,jb}^c + T_{ia,kc}^c X_{kc,\ell d}^{(ij)} T_{\ell d,jb}^h, \quad (17)$$

in which the X integrals contain a modified density:

$$X_{kc,\ell d}^{(ij)} = \int \frac{\rho - \psi_i^2 - \psi_j^2}{\rho^2} \psi_k \psi_c \psi_\ell \psi_d. \quad (18)$$

This theory has the pleasing feature of being exact for a single pair, or for any number of non-interacting pairs: in this case IEPA is exact, and the modified OZ equation results in $\mathbf{T}^h = \mathbf{T}^c$. On the negative side it has a high computational cost ($\mathcal{O}(o^4 v^3)$ for the multiplication in Equation (17)) and although this can be reduced by density fitting we will consider a much simpler approach. Given that in general one expects correlation effects to be dominated by ‘diagonal’ excitations (double excitations from the same doubly-occupied orbital), one can approximate Equation (17) by keeping the original form of Equation (6) but with the definition

$$X_{kc,\ell d} = \int \frac{\rho - \psi_k^2 - \psi_l^2}{\rho^2} \psi_k \psi_c \psi_\ell \psi_d. \quad (19)$$

This theory, which we will call OZ', is also exact for isolated single pairs, but has much lower computational cost. **It should be noted that both of these forms of the OZ equation break orbital variance; however, we will see later that this has little practical impact.**

3. Numerical tests

To examine graphically the various quantities involved it is convenient to compute intracule quantities. In particular we compute

$$I(u) = T_{ia,jb}(ia|\delta(u - r_{12})|jb) \quad (20)$$

for the various amplitudes involved, so that the integral

$$E = \int_0^\infty du 4\pi u^2 \frac{I(u)}{u} \quad (21)$$

is the corresponding correlation energy. These quantities are shown in Figure 1 for water in a cc-pVTZ basis; all calculations were performed with frozen ($1s^2$) core electrons on non-hydrogen atoms.

The basic structure of the plots is as follows. The quantities vanish at the origin (because of the Jacobian) and integrate to zero (because $\langle i|a \rangle = 0$). The intracules have a negative region at around 1 bohr, reflecting the avoidance of electron pairs as a result of correlation effects, and a balancing positive region at larger r .

1 More particularly the data reveal several of the features discussed above. In panel
 2 (a) of Figure 1 it can be seen that the MP2 results lie close to CCD, although
 3 not, as discussed above, for entirely the right reasons. It is also clear that IEPA
 4 overestimates the correlation effect, producing a correlation intracule that is around
 5 15–20% too large. In panel (b) the data CCD OZ^{-1} were obtained by setting $\mathbf{T}^h =$
 6 \mathbf{T}^{CCD} and solving the OZ equation (Equation (6)) for \mathbf{T}^c . This has the effect of
 7 *removing* inter-pair correlations. Comparing with CCD OZ^{-1} one can immediately
 8 see that MP2 is completely unsuitable as a model for direct correlation, but IEPA
 9 is rather close.

10 Finally, in panel (c), CCD is compared with results arising from processing MP2
 11 and IEPA amplitudes with the OZ equation. The MP2 OZ result underestimates
 12 the correlation effects (here we have used the OZ equation to fold in inter-pair
 13 correlations, so the resulting underestimation of correlation is a pure symptom of
 14 the use of a one-particle energy spectrum with spuriously high virtual states). On
 15 the other hand IEPA OZ agrees quite closely with CCD, suggesting that if one starts
 16 of with an accurate description of the independent pair correlations, the simple OZ
 17 equation of Equation (6) can effectively incorporate inter-pair correlation effects.

18 The general features are reproduced for many molecules, and further examples
 19 are (more briefly) shown in Figure 2 for aldehyde, ketene, F_2 and H_2 . For hydrogen
 20 IEPA is already exactly equivalent to CCD, and processing the amplitudes with the
 21 (unmodified) Ornstein–Zernike equation introduces spurious many-electron effects
 22 to this two-electron system. This problem does not arise in the two modified OZ
 23 equations (Equation (17) or Equations (6) and (19)).

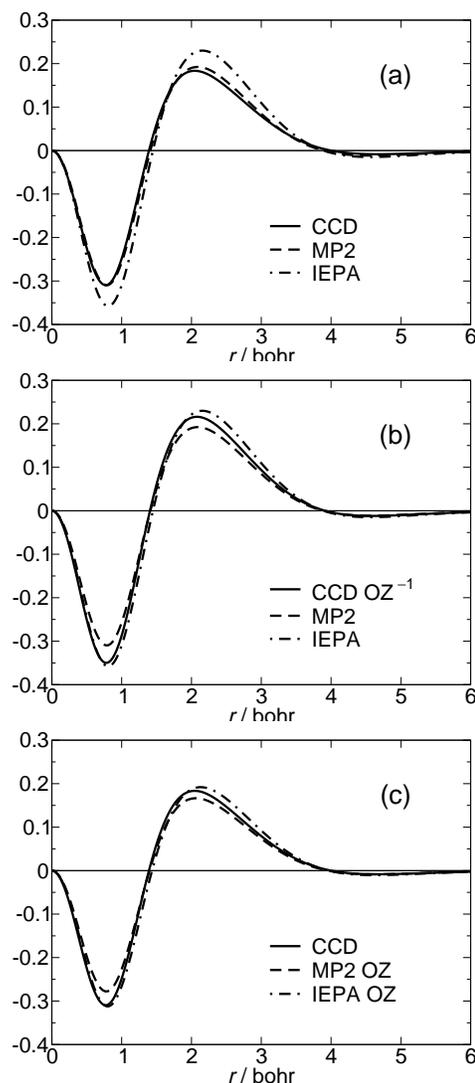
24 25 26 27 28 29 30 **3.1. Correlation energies**

31 To assess the accuracy of correlation energies obtained using the OZ equation we
 32 have performed calculations on selected small molecules. The valence correlation
 33 energies are shown in Table 1. The broad features are that IEPA overestimates
 34 CCD by an average of about 40 millihartree; the uncorrected OZ equation (using
 35 \mathbf{X} as defined in Equation (7)) compensates for this, but often somewhat overshoots;
 36 and the modified OZ equation (using \mathbf{X} as defined in Equation (19)) corrects for
 37 this over-shooting, deviating from CCD by an average of only 2 millihartree. For
 38 comparison MP2 differs from CCD by an average of around 8 millihartree.

39 The systematic over-estimation of correlation energies by IEPA is corrected by
 40 the OZ equation, but as always the spread of the data is also important. Here the
 41 performance is less good, with the standard deviation in the OZ' method relative
 42 to CCD being on the order of 20 millihartree. In considering this result, it should
 43 be noted that the OZ equation certainly has no direct relation to CCD, and the
 44 standard deviation of CCD relative to the more accurate method of CCSD(T)
 45 for these molecules is itself 11 millihartree. Incidentally, it is instructive to look
 46 at the correlation energies per correlated pair: the average error for MP2 valence
 47 correlation energies per pair relative to CCD over all molecules except H_2 is around
 48 1 millihartree. For H_2 the MP2 correlation energy is 7.5 millihartree too small, and
 49 here the true problem with MP2 is revealed: since H_2 has only one pair, there is
 50 no compensation between the use of the 'wrong' denominators and the neglect of
 51 inter-pair correlations.

52 IEPA is not invariant to unitary rotations amongst the occupied orbitals. It is
 53 therefore obvious to ask how the results vary with different representations of the
 54 occupied space, and in particular whether the results are improved using localized
 55 orbitals. All calculations have therefore been repeated with Boys [19] and Pipek-
 56 Mezey [20] localized orbitals, and the data are presented in Table 2. First, as

Figure 1. Comparison of correlation intracules $4\pi r^2 I(r)$ for water in cc-pVTZ with several correlation methods. Panel (a): comparison of CCD, MP2 and IEPA. The MP2 correlation intracule closely agrees with that from CCD, but correlation effects in IEPA are clearly overestimated. Panel (b): comparison of MP2 and IEPA with the direct correlation intracule obtained by processing the CCD amplitudes using the OZ equation in reverse. Panel (c): comparison of the CCD correlation intracule with intracules obtained by processing MP2 and IEPA through the OZ equation.



has been previously observed, we note that with local orbitals IEPA correlation energies are even more overestimated than with canonical orbitals [21]. With Boys localized orbitals, the mean signed error in IEPA relative to CCSD(T) is -74.2 millihartree; the OZ equation reduces this to just -9.6 millihartree, with a standard deviation of around 9 millihartree. With Pipek-Mezey orbitals, the agreement is even better, with a mean signed error of -4.8 millihartree and a standard deviation around 6 millihartree. IEPA followed by the OZ equation agrees more closely with CCSD(T) than does CCSD, which has a mean error and standard deviation of $+20$ millihartree and 9 millihartree for the same set of molecules.

The modified OZ' method does not perform so well, with correlation energies typically falling about halfway between IEPA and unmodified OZ results. The spread of errors is also increased with OZ', indicating that the approximate treatment suggested Equation (19) does not perform particularly well. Implementation and testing of the full theory corrected for spurious inter-pair correlations (Equa-

Figure 2. Correlation intracules $4\pi r^2 I(r)$ for four small molecules using a cc-pVTZ basis and the correlation methods CCD (solid), IEPA (dot-dash) and IEPA-OZ (dash). Panels show intracules for (a) acetaldehyde, (b) fluorine molecule (c) ketene and (d) hydrogen molecule. Note that for H_2 CCD and IEPA are exactly equivalent.

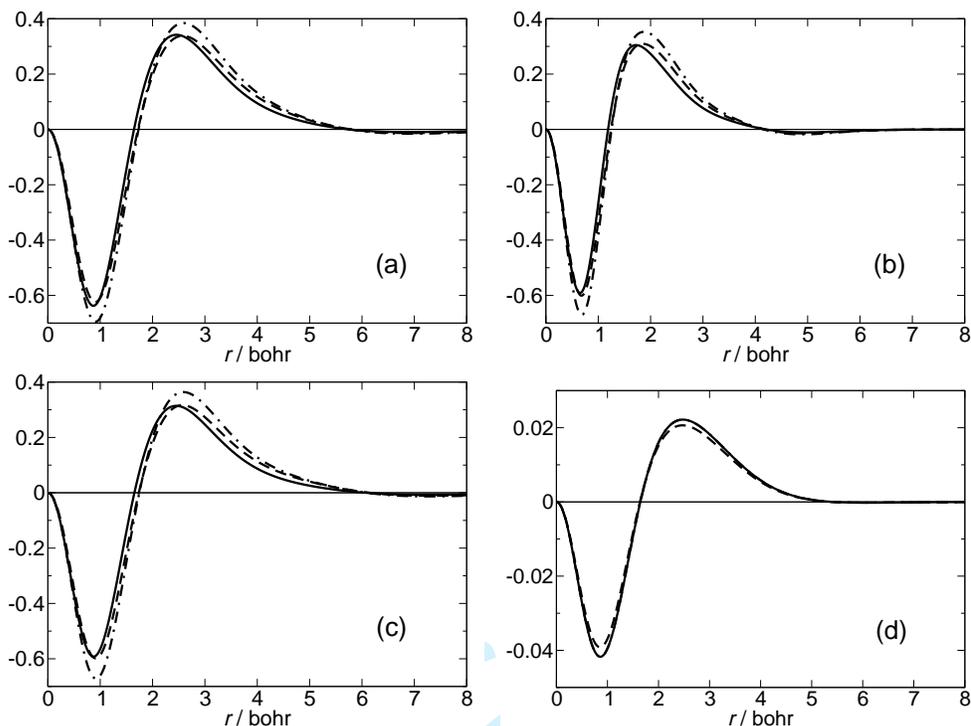
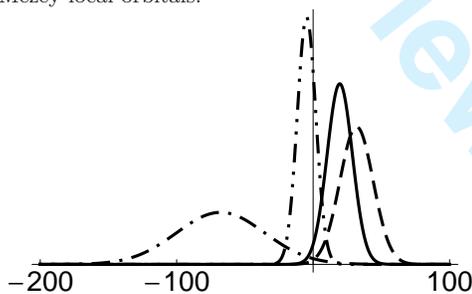


Figure 3. Probability distribution functions for valence correlation energies for the molecules in Tables 1 and 2 relative to CCSD(T)/cc-pVTZ. The horizontal axis is marked in millihartree, and the data presented are for CCSD (solid), MP2 (dashed), IEPA (dot-dash) and OZ (dot-dot-dash). The IEPA and subsequent OZ calculations used Pipek-Mezey local orbitals.



tion (17)) will be investigated in the future.

In any case, the OZ equation does appear to do a reasonable job of correcting IEPA for inter-pair correlations. For further striking evidence one can view the statistics graphically (Figure 3). IEPA using Pipek-Mezey orbitals followed by the OZ equation is closer to CCSD(T) than is CCSD.

4. Conclusions

The Ornstein-Zernike equation connects the direct correlation function to the full correlation function of a fluid. A simple physical argument leads to the equation if ‘direct correlation’ is taken to mean correlation within a single pair of particles, neglecting all others. The electronic structure theory that corresponds to that de-

Table 1. Valence correlation energies (in millihartree) in the cc-pVTZ basis for small first-row molecules using a variety of correlation treatments. OZ and OZ' refer to the OZ equation applied to IEPA amplitudes using \mathbf{X} defined in Equations (7) and (19), respectively. The mean error and standard deviations are relative to CCD.

Molecule	MP2	IEPA	OZ	OZ'	CCD
C ₂ H ₂	-310.9	-362.5	-316.5	-332.3	-319.7
C ₂ H ₄	-335.5	-374.1	-337.7	-348.0	-357.5
C ₂ H ₄ O	-575.7	-635.5	-574.0	-587.1	-590.0
C ₂ H ₅ OH	-602.0	-644.0	-583.0	-594.4	-627.5
C ₂ H ₆	-370.0	-395.6	-361.2	-368.9	-399.4
CH ₃ CHO	-568.3	-630.1	-566.5	-581.5	-583.4
CH ₃ OH	-428.3	-471.2	-423.3	-434.8	-444.5
CH ₄	-198.2	-222.3	-201.9	-208.4	-217.6
CO	-356.8	-427.6	-375.4	-394.4	-355.3
CO ₂	-603.7	-660.7	-586.0	-601.5	-586.5
H ₂	-31.7	-39.2	-36.8	-39.2	-39.2
H ₂ CCO	-540.3	-609.4	-544.1	-560.7	-542.7
H ₂ O	-261.8	-301.5	-264.3	-278.4	-266.6
H ₂ O ₂	-497.3	-558.4	-495.7	-509.3	-500.9
HCHO	-396.2	-454.7	-404.3	-419.6	-402.3
HCONH ₂	-604.5	-669.0	-599.4	-615.6	-609.2
HCOOCH ₃	-800.8	-861.6	-777.7	-792.8	-809.2
HCOOH	-630.8	-689.5	-616.6	-632.0	-629.1
HNCO	-579.6	-659.9	-584.8	-604.9	-569.7
NH ₂ CONH ₂	-809.8	-873.0	-785.1	-802.5	-816.4
NH ₃	-235.1	-271.5	-240.7	-252.9	-246.7
Mean error	8.4	-42.8	11.3	-2.2	—
Std. deviation	11.1	25.9	16.3	18.4	—

description is the independent-electron-pair approximation. IEPA overestimates the correlation energy substantially, but if the IEPA amplitudes are processed through an OZ equation, the correlation energies obtained are much closer to coupled-cluster values.

One can interpret the OZ energy expression diagrammatically. Using dots to denote the \mathbf{X} integrals, a solid line for the IEPA amplitudes and dashes for exchange integrals, the OZ (or OZ') energy expression can be written as

$$E^h = \left(\text{ring diagram 1} \right) + \left(\text{ring diagram 2} \right) + \left(\text{ring diagram 3} \right) + \dots \quad (22)$$

From this expansion it is clear that the energy expression is topologically a sum of ring diagrams. In other contexts this kind of structure has the effect of incorporating some part of the inter-pair correlation to all orders.

The method described in this paper has numerous theoretical deficiencies, some of which are listed below:

- (1) The OZ equation for which there is a clear physical argument contains 2-particle densities, not amplitudes. The use of amplitudes is justified only for MP2 (because the amplitudes provide directly the first-order contribution the 2-particle density). Even if two-particle densities were used, there is no straightforward procedure for extracting the correlation energy.
- (2) If amplitudes are used in the OZ equation, then the density ρ that appears in the integral term should probably be more properly considered as a density

Table 2. Valence correlation energies (in millihartree) in the cc-pVTZ basis for small first-row molecules using a variety of correlation treatments. IEPA and IEPA plus OZ equation were performed using Boys and using Pipek-Mezey localized orbitals, and errors are relative to CCSD(T).

Molecule	CCSD(T)	Boys		Pipek-Mezey	
		IEPA	OZ	IEPA	OZ
C ₂ H ₂	-339.3	-395.3	-341.8	-383.4	-333.8
C ₂ H ₄	-374.9	-422.3	-377.3	-416.7	-373.2
C ₂ H ₄ O	-618.2	-710.5	-635.8	-705.6	-632.0
C ₂ H ₅ OH	-653.2	-738.0	-660.1	-735.6	-658.2
C ₂ H ₆	-414.5	-458.1	-413.4	-458.1	-413.4
CH ₃ CHO	-612.6	-702.7	-625.6	-693.9	-619.0
CH ₃ OH	-461.6	-522.5	-465.2	-520.0	-463.4
CH ₄	-224.7	-244.8	-221.0	-244.8	-221.0
CO	-376.7	-443.4	-387.3	-434.5	-380.9
CO ₂	-622.5	-732.5	-642.4	-720.6	-633.3
H ₂	-39.3	-39.2	-36.8	-39.2	-36.8
H ₂ CCO	-574.9	-667.7	-591.1	-655.6	-581.8
H ₂ O	-275.4	-314.6	-274.5	-312.4	-272.9
H ₂ O ₂	-523.2	-613.3	-539.1	-604.0	-532.1
HCHO	-422.9	-490.6	-433.5	-481.5	-426.6
HCONH ₂	-640.7	-738.3	-655.3	-729.8	-648.7
HCOOCH ₃	-850.8	-980.2	-874.1	-970.5	-866.6
HCOOH	-661.6	-768.1	-679.2	-758.5	-671.8
HNCO	-605.3	-708.6	-623.6	-698.5	-615.8
NH ₂ CONH ₂	-857.3	-986.0	-876.1	-978.9	-870.6
NH ₃	-255.3	-286.9	-253.2	-286.8	-253.2
Mean error	—	-74.2	-9.6	-67.8	-4.8
Std. deviation	—	35.2	8.8	32.3	6.4

of excitations, and the whole theory be considered as a theory of a fluid of (bosonic) excitons $i \rightarrow a$.

(3) We have made no consideration of spin. A proper treatment of spin would presumably further increase accuracy, and will be investigated in the future.

Despite these shortcomings we believe that the evidence provided shows three conclusions very clearly. First the OZ equation can be applied to the electrons in a molecule, because there is nothing particular to classical systems or to systems at finite temperature in the physical argument presented in the Introduction. Second, IEPA is a reasonable model for direct correlation, as defined by the OZ equation. This conclusion is equivalent to saying that the OZ equation appears to be a reasonable approach for incorporating inter-pair correlations. Lastly, the accuracy of MP2 arises from a compensation between the underestimation of pair-correlation energies and the overestimation arising from the neglect of inter-pair correlations.

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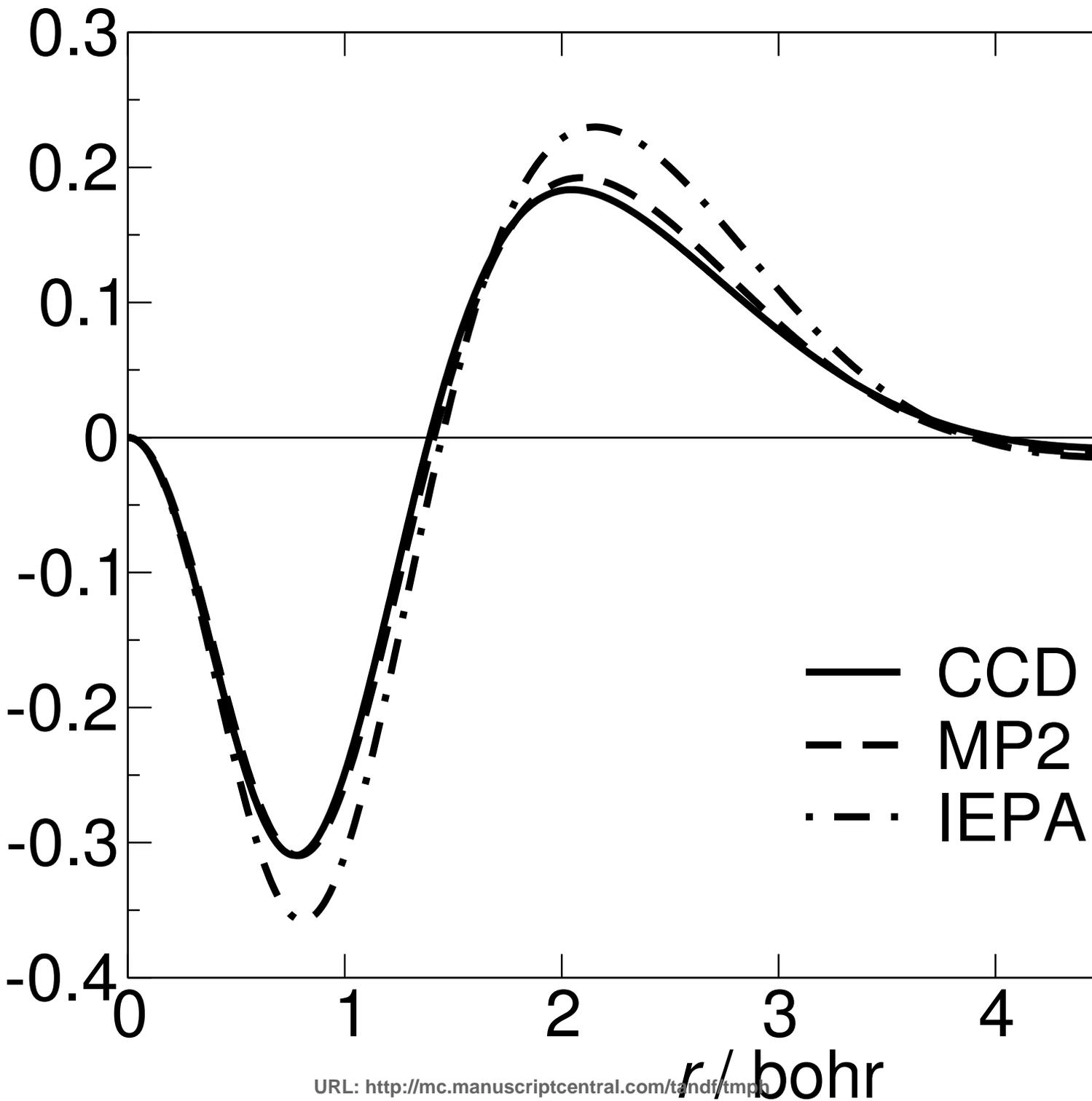
1 that trip and numerous insights on this project are very gratefully acknowledged.

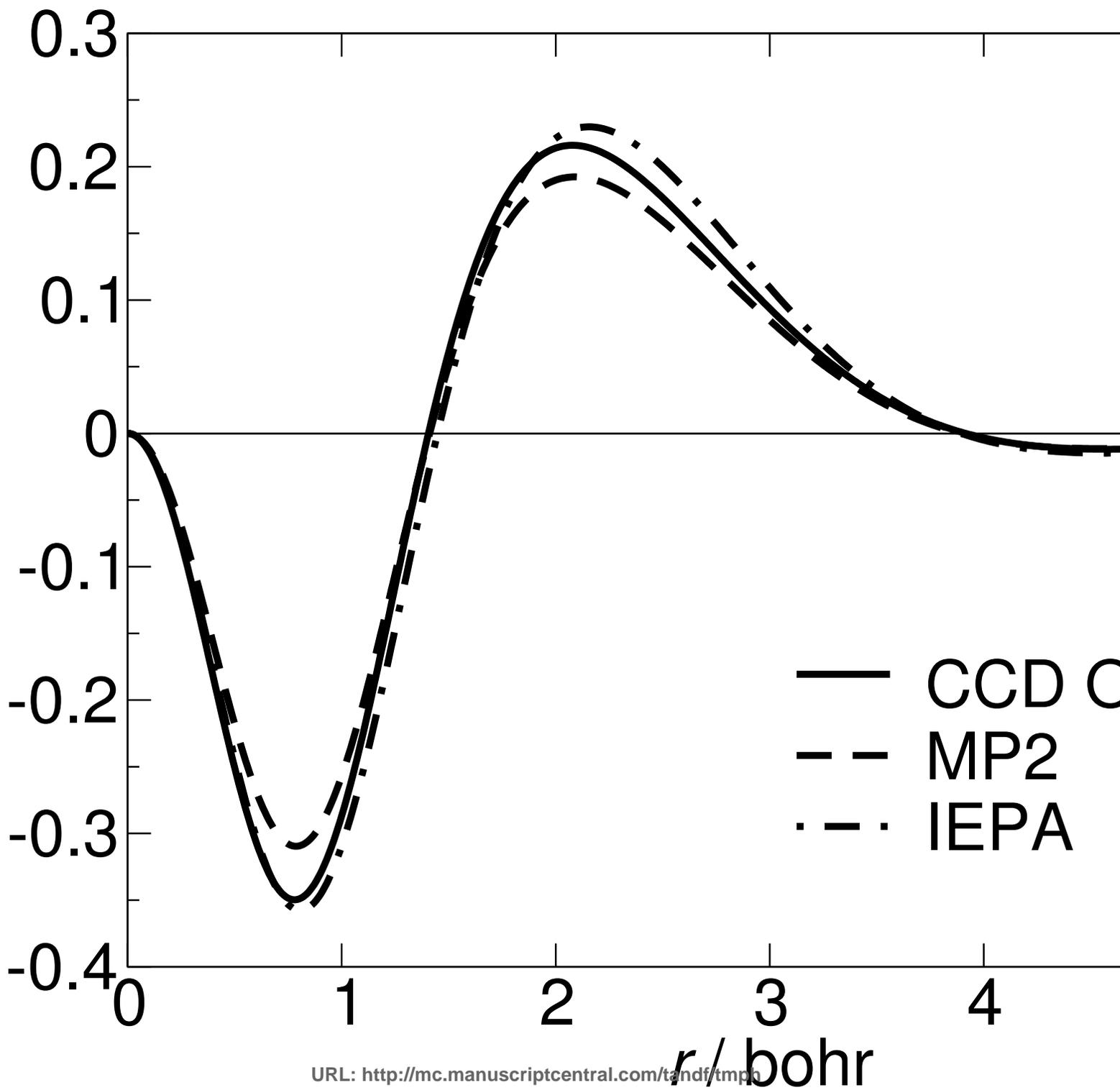
2 We are very grateful to Prof Hans-Joachim Werner for converting the CCSD
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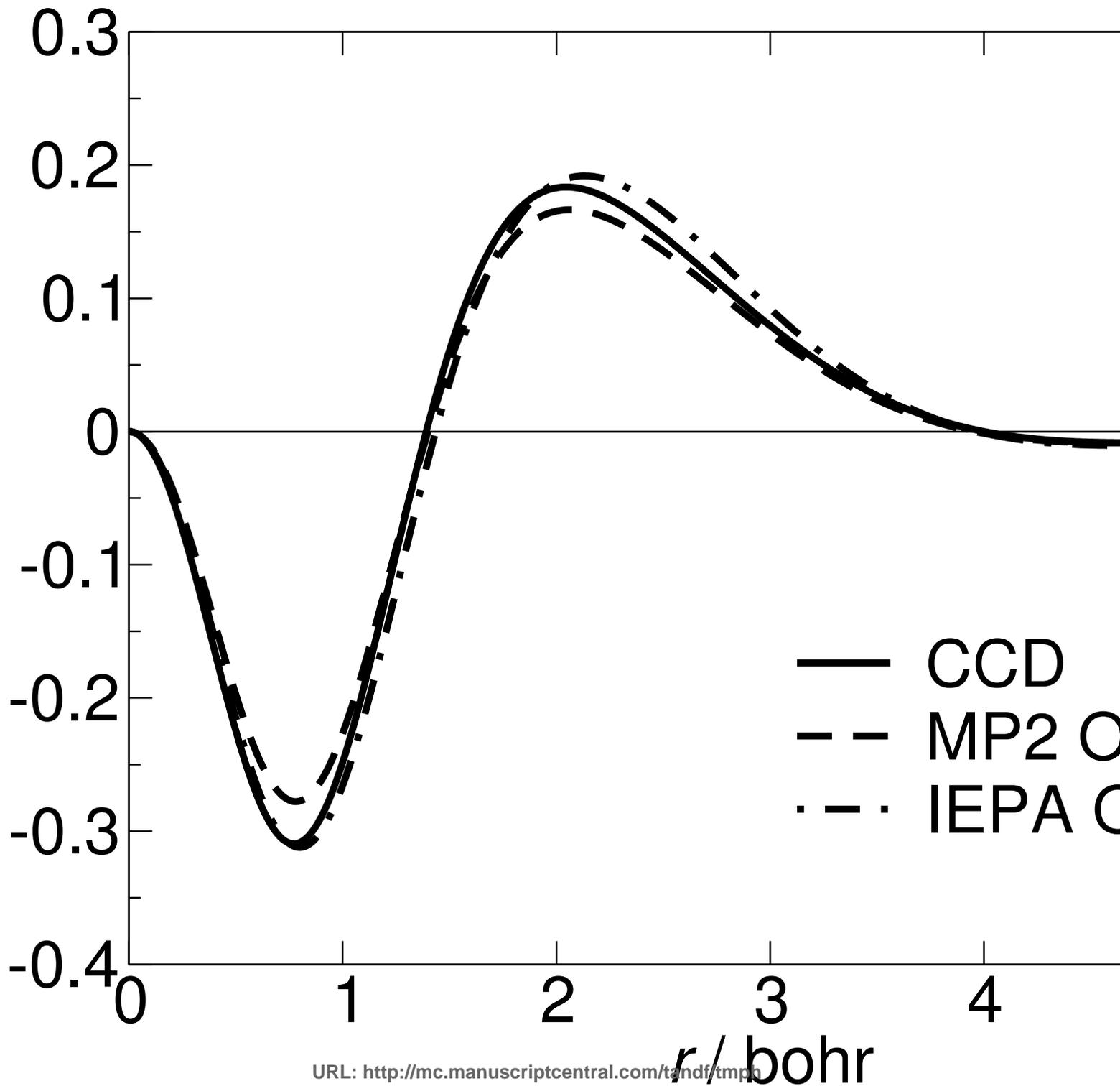
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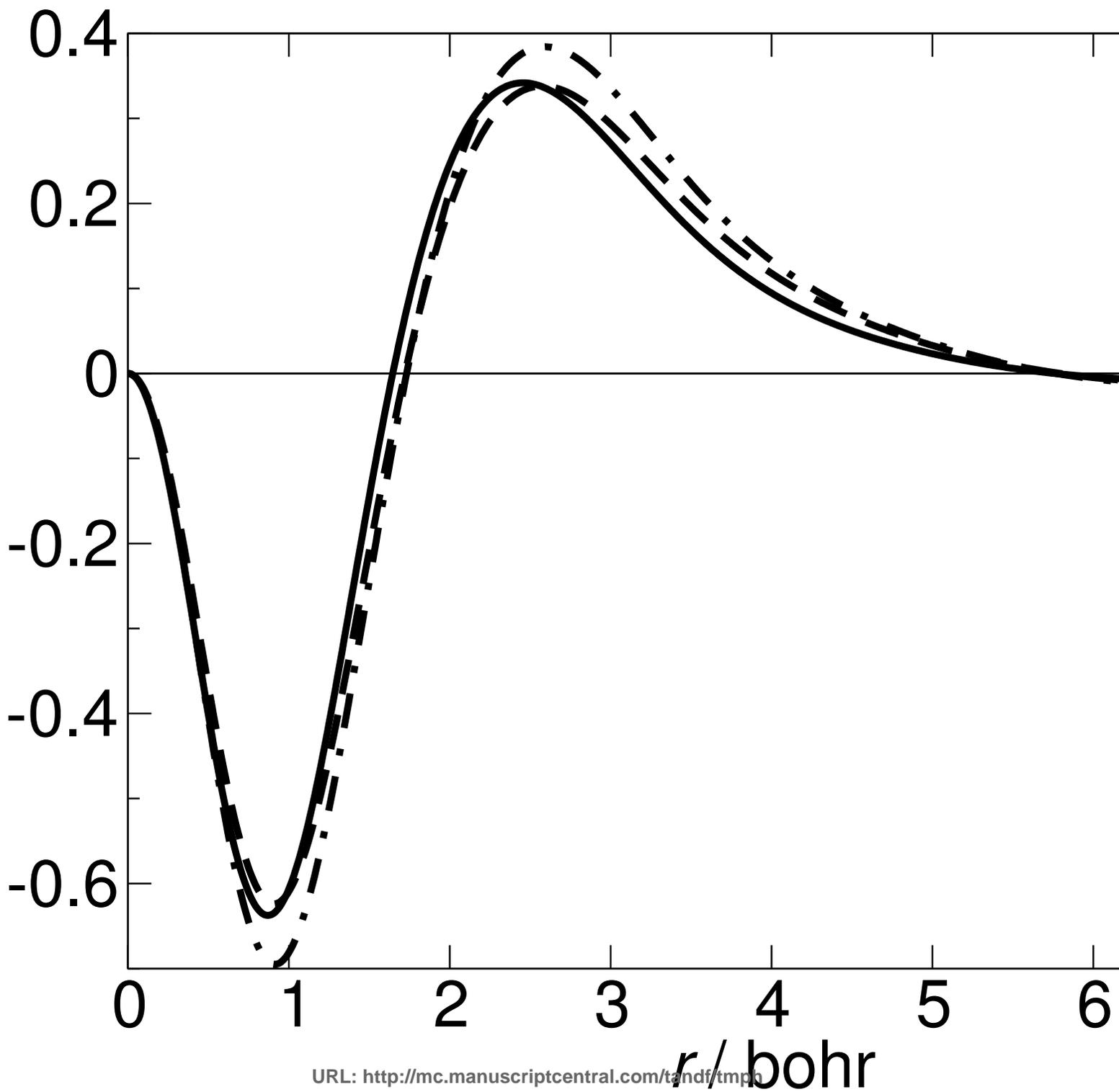
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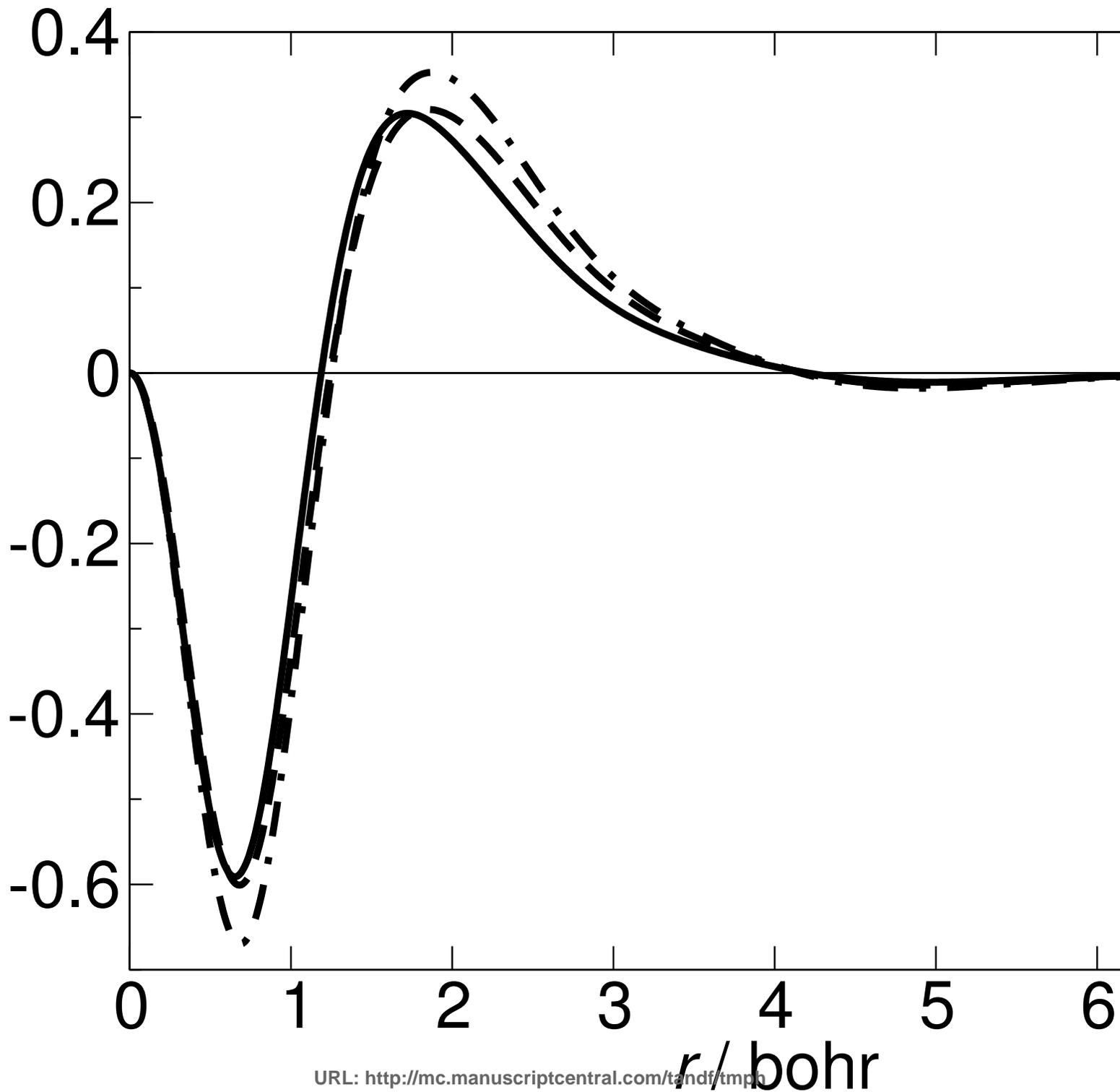


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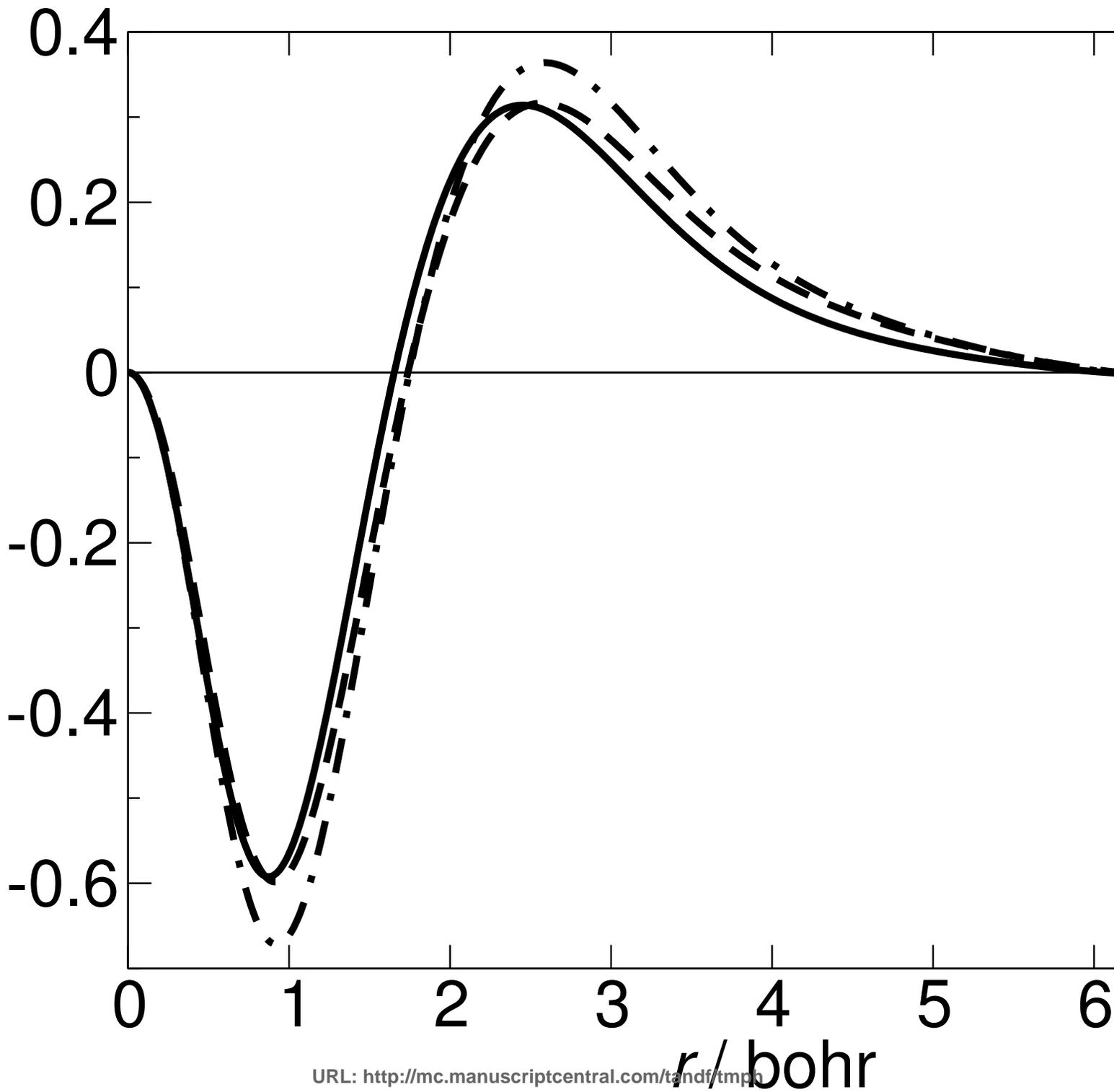




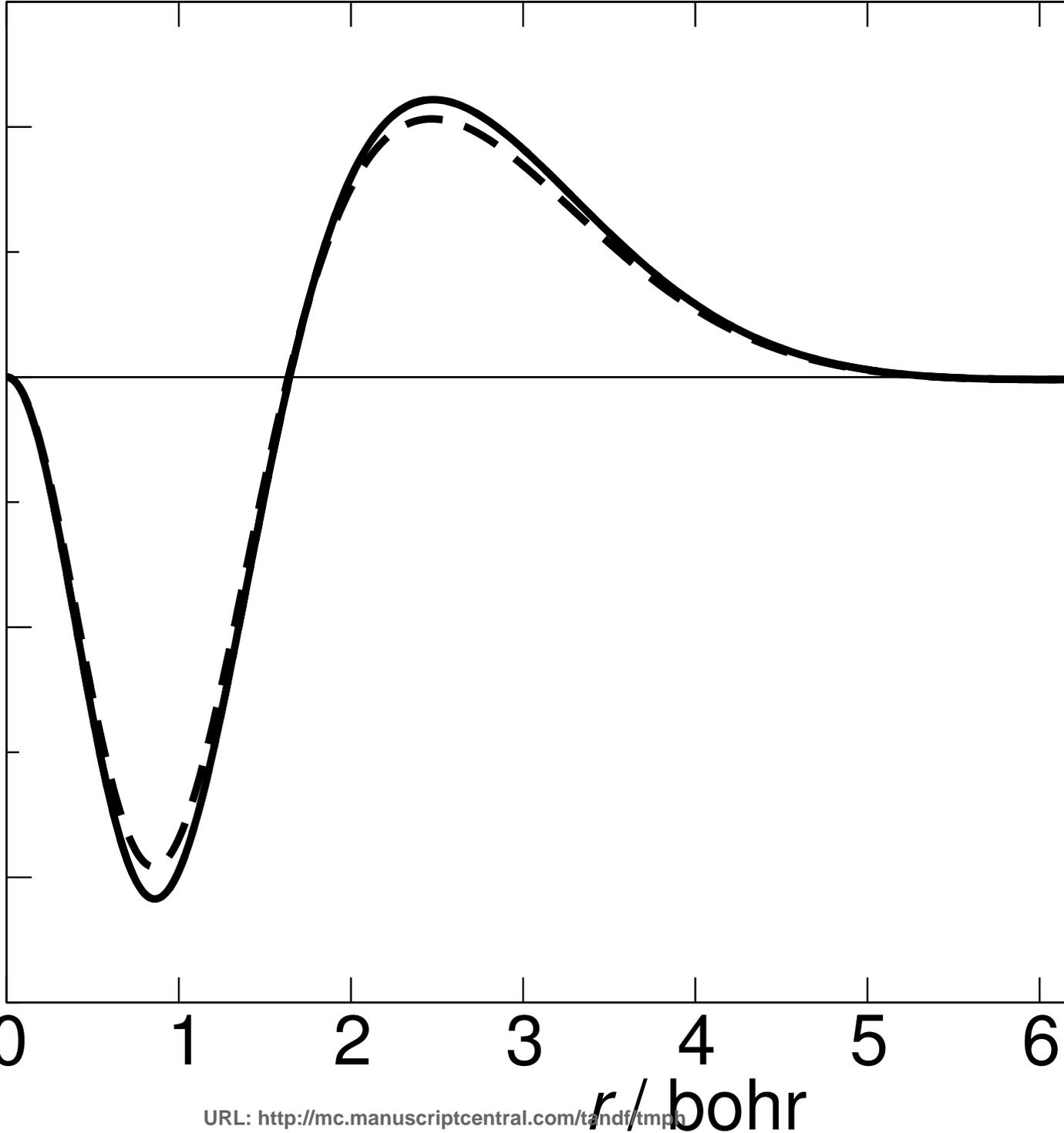
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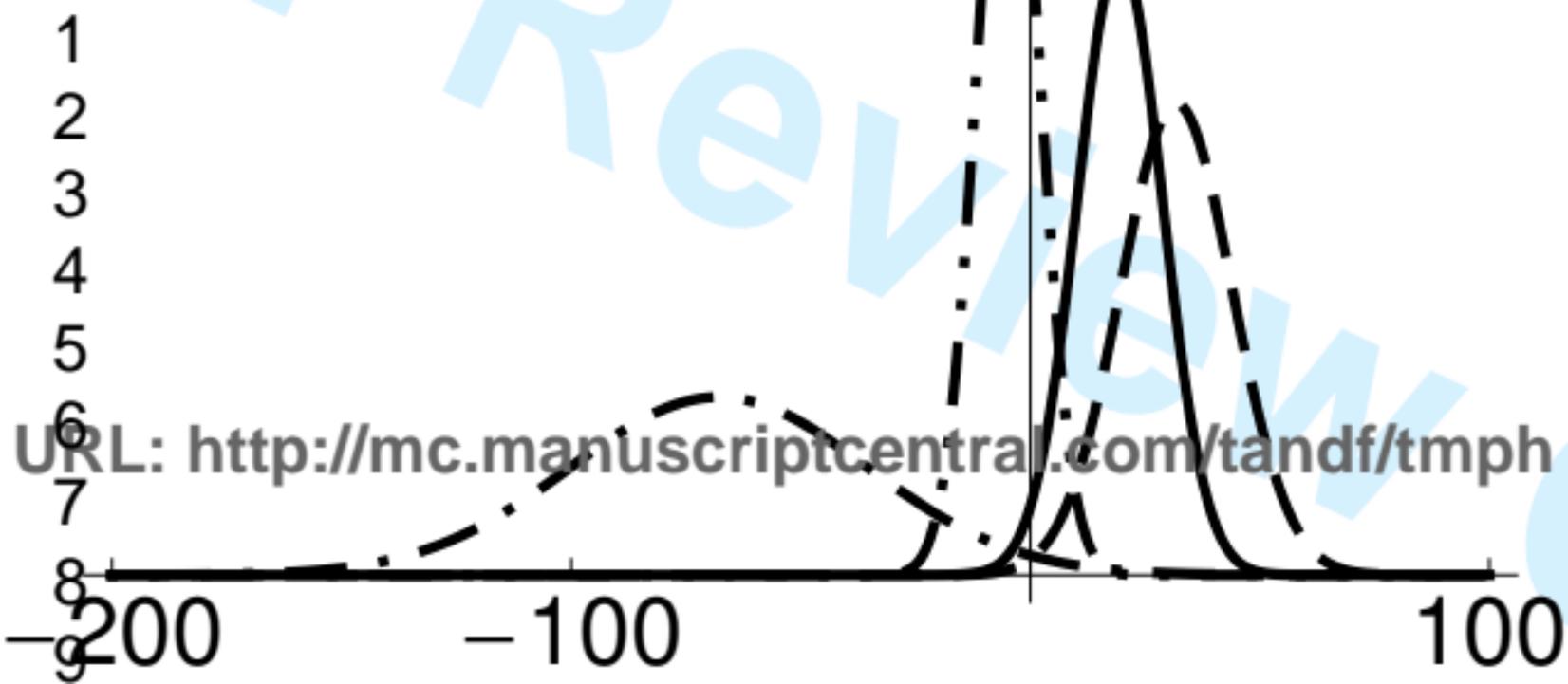


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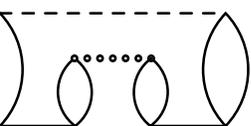
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