



Extrapolating the correlation energy

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Received 3 February 1999; in final form 26 April 1999

Abstract

We present a general scheme for calculating the correlation energy in molecular systems by extrapolation of an energy expression, $E(t)$, obtained from a modified Hamiltonian whose range is reduced to induce localization of the physical interactions. The variable t is introduced such that one recovers the physical system for $t=0$ and $E(t)=0$ for $t \rightarrow \infty$. We show that very accurate correlation energies can be extrapolated at the MP2 level of theory using rational approximations to $E(t)$ based on few evaluations of the energy function. Thus, if localization can be exploited to substantially reduce the computational cost and scaling of the energy evaluation, the scheme becomes a practical tool for large molecular applications. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Within the last decade, alternative procedures for obtaining the MP2 energy have been put forward. Among the most successful are the iterative scheme, the Choleski decomposition of the 4-center 2-electron repulsion integrals, and the Laplace transform of the energy denominator. The first two give rise to the local MP2 [1] and resolution-of-the-identity MP2 [2] methods, respectively, whereas the latter yields a non-iterative atomic orbital–MP2 formalism [3,4]. The underlying motivation for these alternative formulations is the desire to curb the computational cost involved in including electron correlation. We have recently shown that the Laplace AO–MP2 energy can be obtained with a computational work that scales linearly with system size [5], albeit with a cost

multiplier arising from a one-dimensional quadrature. We and others [4–7] have shown that less than ten integrand evaluations are usually required in this quadrature for the accuracy normally required in practical calculations.

In the Laplace ansatz, the integrand is constructed from exponentially weighted molecular orbitals. The weight varies between one and zero and is directly related to the integration variable (see below). As the weight decreases, so does the computational effort needed to evaluate the integrand. Moreover, for large systems with a significant HOMO–LUMO gap where long-range interactions can be efficiently screened, the scaling of the Laplace–MP2 method becomes quadratic, much less steep than that of the conventional procedure, and ultimately linear [5]. Nevertheless, carrying-out the quadrature with accuracy requires evaluating the integrand when the weights remains close (but not exactly equal) to one, thus making the prefactor for the computational cost of

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the Laplace–MP2 method relatively large. Ideally, one would want to evaluate the integrand only when the weights are close to zero.

Independently, renewed interest has been directed towards the adiabatic connection in density-functional theory [8–14]. In its most simple interpretation, it links the physical system and the Kohn–Sham non-interacting reference system via a coupling constant integration λ [8,9]. The Hamiltonian becomes a function of λ and the exchange-correlation energy is obtained by integrating the derivative of the energy with respect to λ over the interval [0,1].

$$E_{xc}[\rho] = \int_0^1 \frac{\partial E_{xc}[\rho, \lambda]}{\partial \lambda} d\lambda. \quad (1)$$

This formula, apparently due to Pauli, has been known for a long time [15] and has also been applied for other iso-electronic processes under the name of ‘integrated Hellman–Feynman’ formulas (see, e.g., Ref. [16]).

There are in fact similarities between the Laplace method and the adiabatic connection. In both cases, there is a smooth function that connects the correlation energy of the physical system (exponential weight equal to one for the Laplace method) and that of the non-interacting system (exponential weight equal to zero for the Laplace method). In both cases, the correlation energy is obtained by quadrature.

In continuation to our previous work on these two subjects [5,14], we are seeking to establish the basis for a new approach for obtaining the correlation energy. Instead of integration (e.g., quadrature), we propose to obtain the correlation energy by extrapolation. The Hamiltonian, and therefore the energy, is made a function of a variable t . For $t = 0$, we have the Hamiltonian for the physical system and for $t \rightarrow \infty$ we have the Hamiltonian for the non-interacting system. Instead of integrating the Jacobian over the $[0, \infty]$ interval, we propose to evaluate the energy at a series of discrete t -values greater than zero and extrapolate the energy for t equal to zero to obtain the correlation energy of the physical system. That is, we want to extrapolate the energy of a fully interacting system (i.e., computationally demanding) using the results obtained for less interacting systems (i.e., computationally manageable).

Whereas there is little doubt that the correlation energy for modified Hamiltonians can be used to

derive the energy for the true Hamiltonian, we will show that accurate energies can be obtained using moderate order extrapolation while considering relatively large t -values, thus making the extrapolation technique a viable alternative to quadrature or conventional schemes for obtaining the correlation energy.

In closing this introduction, we would like to point out that our extrapolation scheme bears no connection to other methods which extrapolate the correlation energy at the basis set limit using a series of calculations [17].

2. Background

Using the Laplace transform of the energy denominator, the canonical MP2 energy for a closed-shell system is given by [3]

$$E_{\text{MP2}} = - \sum_{ij}^O \sum_{ab}^V \int_0^\infty (ia|jb)[2(ia|jb) - (ib|ja)] e^{-\Delta_{ijab}t} dt, \quad (2)$$

$$\Delta_{ijab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j.$$

As usual, i and j denote two of the O occupied molecular orbitals (MO), a and b denote two of the V virtual MOs and ϵ denotes the corresponding Fock eigenvalue. Effectively, the MOs in Eq. (2) become a function of the integration variable t . Given a Fermi level, ϵ_F , the Laplace energy can be written as

$$E_{\text{MP2}} = - \sum_{i'a'j'b'} \int_0^\infty (i'a'|j'b')[2(i'a'|j'b') - (i'b'|j'a')] dt, \quad (3)$$

where i' and a' are the exponentially weighted canonical MOs

$$i' = ie^{(\epsilon_i - \epsilon_F)t/2}; \quad a' = ae^{-(\epsilon_a - \epsilon_F)t/2}. \quad (4)$$

However, the Laplace MP2 energy expression is just a particular case of the more general integral form of Eq. (5)

$$E_{\text{MP2}} = \int_0^\infty - \frac{\partial E_2(t)}{\partial t} dt + E_2(\infty), \quad (5)$$

where we request

$$\lim_{t \rightarrow \infty} E_2(t) = 0, \quad (6)$$

$$\lim_{t \rightarrow 0} E_2(t) = E_{\text{MP2}}. \quad (7)$$

In the case of the Laplace MP2, the function $E_2(t)$ takes the following form.

$$E_2(t) = - \sum_{iajb} (ia|jb) [2(ia|jb) - (ib|ja)] \frac{e^{-\Delta_{ijab}t}}{\Delta_{ijab}}. \quad (8)$$

Fig. 1 shows $E_2(t)$ for the water molecule using the cc-pVDZ basis set. The amount of correlation energy, as measured by Eq. (8), is a milli-hartree or less for t greater than approximately 1.2 au. Clearly, as t increases, only the energy levels closer to the Fermi level have a significant contribution to the energy and the effective number of $ijab$ quartets decreases. Evaluating $E_2(t)$ for large t can be made to require significantly less computational effort than evaluating $E_2(t)$ for $t = 0$. For all practical purposes, there is no correlation energy for t -values greater than $t = 3$ au.

Using Eq. (5) as a departure point rather than the Laplace transform, it is clear that one is not limited to the form shown in Eq. (8) and that many different function forms could be used for obtaining the correlation energy. Indeed, one could tailor a function form for specific purposes (see, e.g., Ref. [14]) while still being able to obtain the exact correlation energy. Moreover, implementation of the Laplace–MP2 method has shown that decisive computational advantages can be gained over the traditional approach.

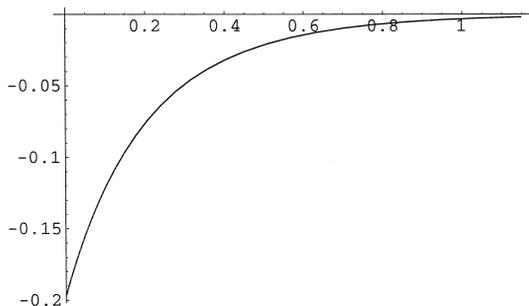


Fig. 1. MP2/cc-pVDZ correlation energy as a function of t (see Eq. (8)) for water.

The other point we want to highlight is that one is not limited to an integral form but that the correlation energy can be obtained by extrapolation as Eq. (7) suggests. Clearly, this would apply to any function of the correlation energy $E_2(t)$, provided that $E_2(t)$ verifies

- $E_2(t)$ and its derivatives are continuous over $t \in [0, \infty)$,
- $E_2(0) = E_{\text{MP2}}$,
- $\lim_{t \rightarrow \infty} E_2(t)$ is finite.

One can already foresee that smooth monotonic functions connecting the fully interacting system to the non-interacting ($E_2(\infty) = 0$) system would be good candidates. Here for the sake of generality, we are assuming that the less interacting the system is, the less computationally demanding it is to evaluate the energy function or its Jacobian.

Throughout our discussion, and specifically in Eq. (5), we have used the MP2 method mainly because of its simplicity. The arguments, though, can be easily generalized to any other ab initio correlated method. They amount to modifying the Hamiltonian to make it a function of the variable t . Once a suitable modified form for the Hamiltonian is chosen, the correlation energy for any method, including sophisticated methods such as coupled-cluster, can be obtained via either quadrature or extrapolation.

In this work, we focus exclusively on obtaining the correlation energy by means of extrapolation. We show that the issue is not whether the extrapolation approach works, but rather how well it does work. Clearly, the extrapolation approach would not be viable if either a large number of function evaluations or evaluating $E_2(t)$ close to $t = 0$ (i.e., considering the fully interacting system) is required or if the accuracy could not be controlled.

3. Test functions

As mentioned above, there is a vast ensemble of functions to choose from. Some will offer better insight and others will be more amenable to computational efficiency. We will not examine here the merits of specific functions or modifications to the Hamiltonian. Rather, we examine the extrapolation of a prototypical correlation energy function $E_2(t)$ whose magnitude decays with increasing t . In other

words, we focus on energy functions as that depicted in Fig. 1.

Considering modifications of the zeroth order Hamiltonian, H_0 , has the advantage of being conceptually simple and revealing. This type of modification affects the energy denominator in the MP2 energy expression and each of the $(OV)^2$ contributions to the energy now depends on t .

$$H_0 = \sum_i^o |i\rangle \langle i| \mathbf{F} |i\rangle \langle i| + \sum_a^v |a\rangle \langle a| \mathbf{F} |a\rangle \langle a|. \quad (9)$$

We consider these test functions as ‘Litmus test’. Assessing the quality and robustness of the extrapolation technique using such simple model Hamiltonians is a necessary first step before considering modifications to the two-body part (e.g., the Coulomb part) of the Hamiltonian. Furthermore, modifying the 4-index energy denominator of the MP2 expression and extrapolating the resulting correlation energy has many things in common with modifying the 4-center Coulomb integrals. In the present work, we have considered modifying H_0 in such a way that the virtual energy levels are uniformly or non-uniformly shifted. Of course, such modifications do not alter the first-order perturbation theory energy (i.e., the Hartree–Fock energy). The results presented here are obtained using a development version of the Gaussian suite of programs [18].

3.1. Uniform shifting of the orbital energy levels

For a uniform shifting of the energy levels, a function of the energy can be written as

$$E_2(t) = - \sum_{iajb} (ia|jb) [2(ia|jb) - (ib|ja)] \frac{1}{\Delta_{ijab} + t}. \quad (10)$$

This function may be seen as the MP2 energy for $H_0(t)$

$$H_0(t) = \sum_i |i\rangle \langle i| \mathbf{F} |i\rangle \langle i| + \sum_a |a\rangle \langle a| \mathbf{F} |a\rangle \langle a| + t|a\rangle \langle a|, \quad (11)$$

that is, the MP2 energy with the HOMO–LUMO gap increased by $t/2$ hartree. We point out that this

type of Hamiltonian has already been studied within the scope of density functional theory [14]. Furthermore, this Hamiltonian in conjunction with an extrapolation technique can become a practical tool for obtaining the correlation energy of systems with HOMO–LUMO gaps close to zero.

Clearly, the correlation energy function satisfy all three properties mentioned above: it is smooth over the $[0, \infty]$ interval, the canonical energy is obtained at $t = 0$ and it has a finite asymptote for large t . The challenge consists in extrapolating the sum of a large number of functions with different rates and magnitudes. Given a number of data points, the extrapolation can be carried out using either a polynomial form,

$$E_2(t) \approx \sum_i^n a_i t^{i-1}, \quad (12)$$

or a rational form,

$$E_2(t) \approx \frac{\sum_i^k b_i t^{i-1}}{\sum_i^l c_i t^{i-1}}. \quad (13)$$

In both cases, the number of free parameters equals the number of data points. Throughout this work, we have used the so-called *diagonal* rational function where the polynomial degree of the numerator is equal to that of the denominator [19]. Fig. 2 shows the error in the extrapolated MP2 energy using both a polynomial extrapolation and a rational extrapolation. The quality of the extrapolation most likely varies with increasing number of Δ_{ijab} . Therefore, for testing purposes, we first have considered a relatively large water cluster containing 10 molecules.

One of the most important aspects of the extrapolation described in this Letter is the number of function evaluations that are needed to achieve a prescribed accuracy. In our experience, the rational extrapolation has proven to be far more successful than the polynomial extrapolation as it requires much less data points to achieve the same kind of accuracy. In fact, just as for the Laplace transform quadrature, μ -hartree accuracy can be achieved by extrapolation using less than 10 function evaluations at properly chosen points (see below). This high degree of accuracy obtained by a moderate order

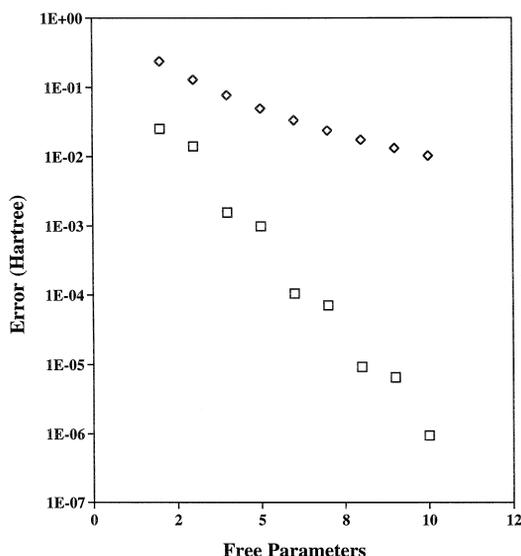


Fig. 2. MP2 energy extrapolation error as a function of the number of free parameters for $(\text{H}_2\text{O})_{10}$. Squares: rational polynomial extrapolation; diamonds: polynomial extrapolation. Abscissa used in extrapolation: $t_i = 2.0 + 0.8i$ hartree.

rational polynomial is remarkable considering that the energy expression of Eq. (10) is itself a rational polynomial of degree $(OV)^2$.

3.1.1. Accuracy for a fixed number of points

One way to judge the robustness of the extrapolation is by examining the error as the t -values that enter the rational polynomial get larger while keeping constant the number of data points. Fig. 3 shows how the 10-point extrapolation error grows with increasing t .¹ Virtually no error is induced when considering shifting the energy levels by only a few hartrees. As shown from Fig. 3, the exact correlation energy can be obtained within less than 1 μ -hartree error when shifting the energy denominator by approximately 5 hartree (i.e., when increasing the HOMO–LUMO gap by 2.5 hartree). Remarkably, even though the HOMO–LUMO gap is shifted by 12 hartree or more, extrapolating the correlation energy to a zero shift induces an error of less than 1 milli-hartree for the relatively large $(\text{H}_2\text{O})_{10}$ cluster.

¹ Given a minimum value for t , t_{\min} , the abscissa are chosen by first uniformly distributing 10 r values over $(\text{Tanh}[\sqrt{t_{\min}}], 1)$. The 10 t -values are then obtained by using $t(r) = \text{ArcTanh}[r]^2$.

In order to further assess the quality and robustness of the rational extrapolation we have used the 55 molecules from the original G2-test set [20,21] using the MP2/6-311 + G(3df,2p) level of theory. This molecular set along with the large basis set offers the possibility to test the extrapolation for a wide variety of HOMO–LUMO gaps, eigenvalue spectrum range and distribution. The extrapolated correlation energy was compared with the exact energy. The average, maximum and rms errors as a function of t_{\min} are presented in Table 1. By in large, what was observed for $(\text{H}_2\text{O})_{10}$ is found to apply for all of the G2 set. Even when for each of the 10 energy points the HOMO–LUMO gap is opened by at least 5 hartree ($t_{\min} = 10$ hartree), the physical correlation energy can be extrapolated with milli-hartree accuracy.

3.1.2. Number of points for a fixed accuracy

A valuable feature of the rational polynomial used here, is that, using the same data points, it is possible to estimate the error for the extrapolated value [19]. The results shown in Table 1 indicate that this error estimate follows closely the actual error. Indeed, this constitutes a reliable a-posteriori diagnostic for the

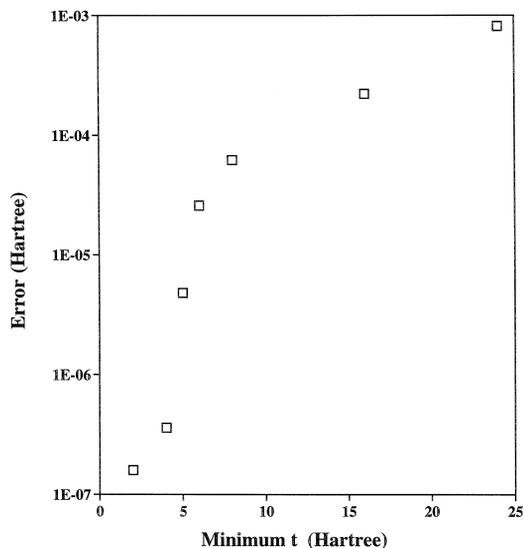


Fig. 3. MP2 energy extrapolation error as a function of the minimum t value used in the extrapolation (see text) for $(\text{H}_2\text{O})_{10}$.

Table 1

MP2 energy extrapolation error and error on estimated error as a function of t_{\min} , the minimum t value used in the extrapolation (see text), for 55 molecules of the G2 set using the 6-311 + G(3df,2p) basis set. All quantities are in hartree

t_{\min}	Actual error			Actual error – estimated error		
	Average	Maximum	RMS	Average	Maximum	RMS
2	4.47×10^{-6}	4.00×10^{-5}	8.44×10^{-6}	1.16×10^{-6}	1.48×10^{-5}	2.67×10^{-6}
5	7.06×10^{-5}	4.33×10^{-4}	1.11×10^{-5}	2.12×10^{-5}	2.90×10^{-4}	5.55×10^{-5}
7	1.82×10^{-4}	9.03×10^{-4}	2.68×10^{-4}	5.65×10^{-5}	5.94×10^{-4}	1.23×10^{-4}
10	3.88×10^{-4}	1.70×10^{-3}	5.23×10^{-4}	1.36×10^{-4}	1.08×10^{-3}	2.39×10^{-4}

quality of the extrapolation. Furthermore, this error estimate can be used to devise a scheme to automatically select t values in order to achieve a required accuracy in the extrapolation, very much as it is done in the Burlisch–Stoer method for integrating differential equations [19].

An automatic selection scheme should satisfy three simple requirements: (1) the value $t = 0$ should never be considered; (2) any degree of accuracy should be achievable; (3) as few and as large t values as possible should be used. Thanks to the robustness of the rational extrapolation, a number of different schemes can be put forward. We propose the following simple iterative scheme. Given k evaluations of $E_2(t)$ and a maximum step-size parameter α , choosing t_{k+1} such that $t_{k+1} \geq \alpha t_k$ with $0 < \alpha < 1$ would satisfy at once conditions 1 and 2. By enforcing that α be less than 1, the t -values geometrically approach zero and the gradual improvement of the rational extrapolation is insured. Condition (3) can be satisfied to some measure by adjusting the value of α . For example, if $t_1 = 10$ hartree and α is set to 0.85, it would take more than 10 evaluations before having to evaluate $E_2(t)$ for t -values less than 2 hartree. Judging from the results presented in Table 1 and Figs. 2 and 3, such a setting would yield an accuracy of 10^{-4} hartree or better in less than 10 function evaluations for most applications. Before evaluating the energy for $t_{k+1} = \alpha t_k$, one can examine the rational approximation obtained with the k data points, and in particular the estimated error at both $t = 0$ and $t = \alpha t_k$. In general, the quality of the rational approximation quickly deteriorates as one considers points further and further outside the sampled region. A large estimated error at these two t values would signify that the sampled abscissa are

too far apart. Therefore, instead of evaluating the energy for $t_{k+1} = \alpha t_k$, we evaluate the energy at a t -value within the interval $(\alpha t_k, t_k)$. This t -value is chosen such that the ratio of the estimated error at this point and at $t = 0$ is less than 10^{-2} . By doing so, not only the t -values are as far as possible from $t = 0$, but the quality of the rational approximation improves with the addition of each new data point.

This simple automatic selection scheme was applied to the extrapolation of the MP2 energy for the G2 set. Table 2 lists the number of points needed to achieve a certain accuracy depending on the starting t -value. It can be seen that for a wide variety of systems, any given level of accuracy can be achieved using a moderate number of data points irrespective of the choice of the starting t -value.

3.2. Non-uniform shift of energy levels

Having demonstrated the robustness of the rational extrapolation for uniform shifts of the orbital energy levels, we now investigate the quality of the

Table 2

Number of points needed to achieve a given MP2 energy extrapolation error as function of the maximum t value used in the automatic selection scheme (see text), for 55 molecules of the G2 set using the 6-311 + G(3df,2p) basis set

$Max(t)$	Error (hartree)					
	$\leq 10^{-3}$	$\leq 10^{-4}$	$\leq 10^{-5}$	$\leq 10^{-3}$	$\leq 10^{-4}$	$\leq 10^{-5}$
	Average number of points			Maximum number of points		
10	6.5	8.2	10.7	8	11	13
7	5.6	7.2	9.6	8	10	12
5	5.0	6.9	8.6	6	9	11

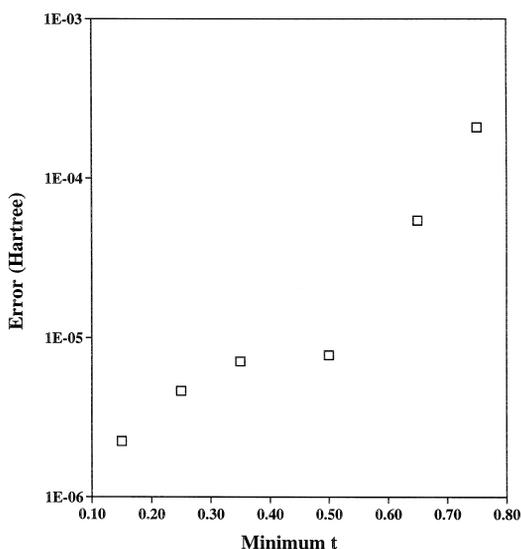


Fig. 4. MP2 energy extrapolation error as a function of the minimum t value used in the extrapolation (see text) for $(\text{H}_2\text{O})_{10}$.

extrapolated energy for non-uniform shifts. The proposed form is

$$E_2(t) = - \sum_{ia|jb} (ia|jb) [2(ia|jb) - (ib|ja)] \frac{1}{\Delta_{ijab} + t(2\theta - \epsilon_a - \epsilon_b)}, \quad (14)$$

where θ is an arbitrary constant energy level. This function has the particularity that for $t = 1$, it amounts to computing the MP2 energy for a system with all virtual energy levels being degenerate at θ . Here, the robustness of the extrapolation can be judged by examining the error when considering t -values taken from the interval (0,1) while setting θ to $\max_a(\epsilon_a)$. The results are shown in Fig. 4. As for a uniform shift of the energy levels, the rational extrapolation proves to be a very robust method even when the eigenvalue spectrum is considerably modified. The rational extrapolation extracts enough information from the repeated ‘squeezing’ of the energy levels to be able to extrapolate the energy of the unmodified system. We observed that the quality and robustness of the rational extrapolation technique using a non-uniform shift is similar to the one observed for the uniform shift. However, as it would be expected, we

point out that the best results are found when the unoccupied eigenvalue range is small.

4. Conclusion

In this Letter we have shown that by making the canonical MP2 correlation energy expression a smooth continuous function of an arbitrary variable, the exact correlation energy can be reliably obtained by low-order extrapolation techniques. This approach is intimately connected to, and generalizes, the Laplace Transform of the MP2 energy which corresponds to the integration of the Jacobian of a specific function. Of the two types of extrapolation, rational and polynomial, the rational extrapolation technique is the most reliable and proves to be very powerful. The function can be made to describe the smooth passage from the fully interacting system to the non-interacting system while highlighting specific physical properties. The correlation energy of the fully interacting system can then be reliably obtained without ever having to examine it directly since it can be extrapolated from the results obtained for model systems with less interactions. By exploiting the robustness of the extrapolation approach, we suggest that the computational cost associated with describing fully interacting systems can be significantly reduced.

Acknowledgements

This work was supported by the National Science Foundation (CHE-9618323).

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