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Correcting model energies by numerically integrating along an adiabatic connection and a link to density functional approximations

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Model Hamiltonians are considered for which electrons interact via long-range forces. It is assumed that their eigenvalues can be obtained with satisfying accuracy. Extrapolation techniques using asymptotic behavior considerations provide estimates for the energy of the physical system. Results for the uniform electron gas and some two-electron systems show that very few quadrature points can already produce good quality results. Connections to the density functional theory are discussed.
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I. INTRODUCTION

Let H be a physical Hamiltonian. A family of model Hamiltonians, $H(\mu)$, parametrized by μ is chosen, such that H is the limit of $H(\mu)$ when μ goes to infinity. $H(\mu)$ is chosen so that solving accurately the corresponding Schrödinger equation can be done with a reasonable amount of effort. This paper explores the possibility of extrapolating the energies obtained for the model Hamiltonians $H(\mu)$ to the limit, physical Hamiltonian, H. This approach is called energy extrapolation (EE).

There are two levels of choice in this method. The first one is that of the model Hamiltonians, the second one is that of the extrapolation technique. The model Hamiltonians have to be chosen so as to keep low the cost of the computation of the eigenvalues needed. The extrapolation techniques chosen in this paper become exact when the dependence on μ of the eigenvalues under consideration can be described in a given basis. This basis can be chosen in accordance with the choice of the model Hamiltonians. Among these extrapolation schemes is numerical integration, not using the interval endpoint corresponding to the physical system.

In order to illustrate the EE method, a model Hamiltonian $H(\mu)$ is chosen identical to that showing up in a density functional approximation (DFA), the local density approximation (LDA), used for (an extension of) the Kohn-Sham system. In the DFA the difference between the energy of the physical system and that of the model system is recovered not by extrapolation, but by using a functional of the density [the one which by functional derivation produced a potential for $H(\mu)$]. Using the same $H(\mu)$ for both EE and the DFA allows to compare the effect of the approximations involved (basis and number of points used for EE, density functional for the DFA). This comparison is made using only a set simple systems, for which accurate results could easily be generated. The numerical results for EE show that a surprisingly small set of points (one or two) are needed to obtain an accuracy comparable or better than the DFA. A way to improve DFAs using the results of the present investigation will also be suggested.

Advantages of EE are: (i) systematic improvement, by addition of points (models), (ii) size-consistency, when a suitable extrapolation technique is used, (iii) applicability to several eigenstates, and not only to the ground state.

This paper only analyzes the errors produced by the extrapolation technique. Error propagation (when extrapolating from the model to the physical system) is left for later studies, as is the study of the possible benefits of solving the Schrödinger equation for the model systems and not for the physical system.

II. APPROACH

A. Principle

In DFAs one solves the Schrödinger equation for a model system (the Kohn-Sham system for a given approximation, e.g., in the LDA). One assumes that this can be done accurately. One needs, however, to know the energy of the physical system, and the correction needed (the difference between the energy of the physical system and the model system) is not known accurately. This problem can be generalized to the case where the model system is more complicated than the Kohn-Sham Hamiltonian, because it contains some interaction between fermions (see, e.g., Ref. 1). Let us formalize it by considering Hamiltonians which we characterize by a variable μ,

$$H(\mu) = T(\mu) + V(\mu) + W(\mu) \tag{1}$$

for which the Schrödinger equation is

$$H(\mu)\Psi(\mu) = E(\mu)\Psi(\mu), \tag{2}$$

where T is a non-local one-particle operator, V is a local one-particle operator, and W is a local two-particle operator. Our convention is that the physical system is obtained when μ is infinite:

$$\begin{aligned} H &\equiv H(\infty) = T + V_{ne} + V_{ee}, \\ E &\equiv E(\infty), \end{aligned} \tag{3}$$

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where $T = T(\infty)$ is the kinetic energy operator, $V_{ne} = V(\infty)$ is the external potential (of the interaction between nuclei and electrons), and $V_{ee} = W(\infty)$ is the potential of the interaction between electrons.

The energy of the physical system, E, is unknown, and even if some $E(\mu)$ can be obtained accurately, we need to correct it by some $\bar{E}(\mu)$ to obtain E:

$$\bar{E}(\mu) \equiv E - E(\mu). \tag{4}$$

This correction is unknown, except trivially $\bar{E}(\infty) = 0$. However, the physical energy is invariant with μ, $E = E(\mu) + \bar{E}(\mu)$, and the change of $E(\mu)$ with μ has to be compensated by a change with an opposite sign in $\bar{E}(\mu)$. Thus, the difference between two values of $\bar{E}(\mu)$ is known, when the difference between the corresponding values of $E(\mu)$ is known:

$$\bar{E}(\mu_1) - \bar{E}(\mu_2) = -(E(\mu_1) - E(\mu_2)). \tag{5}$$

When $E(\mu)$ is differentiable with respect to μ, one can obtain the derivatives of the corrections, $\partial_\mu \bar{E}(\mu) \equiv \bar{E}'(\mu)$, from those of the model systems:

$$\bar{E}'(\mu) = -E'(\mu). \tag{6}$$

These considerations hold also for the higher differences and derivatives.

In order to construct an extrapolation scheme, we will consider that we can expand $\bar{E}(\mu)$ in some basis,

$$\bar{E}(\mu) \approx \tilde{E}(\mu) = \sum_i c_i \chi_i(\mu). \tag{7}$$

One also has for the derivative

$$\bar{E}'(\mu) \approx \tilde{E}'(\mu) = \sum_i c_i \chi_i'(\mu). \tag{8}$$

Knowledge about the dependence of E on μ can be funneled into the basis.

B. Extrapolation techniques

The extrapolation formulas are derived making the assumption that a set of χ_i can be reliably used in Eq. (7). Evaluating Eqs. (7) and (8) at some points μ_k, we obtain a system of equations, linear in the c_i,

$$\sum_i c_i[\chi_i(\mu_k) - \chi(\mu_0)] = \tilde{E}(\mu_k) - \tilde{E}(\mu_0),$$

$$\sum_i c_i \chi_i'(\mu_k) = \tilde{E}'(\mu_k). \tag{9}$$

The number of equations with $\tilde{E}(\mu_k) - \tilde{E}(\mu_0)$ on the rhs is independent from the number of equations with $\tilde{E}'(\mu_k)$ on the rhs, and is a matter of choice. Assuming that some E and E' are known for some μ_k, the c_i can be determined using for the rhs Eq. (5), and/or Eq. (6). Please notice that the c_i become linear combinations of $E(\mu_k)$ and/or $E'(\mu_k)$:

$$c_i = \sum_k a_{ki} E(\mu_k) + \sum_k b_{ki} E'(\mu_k), \tag{10}$$

where the coefficients a, b are determined by the inverse of a matrix containing χ_i and χ_i' at the points μ_k. Once the c_i are known, they can be used to approximate $\bar{E}(\mu_0)$ with Eq. (7):

$$\bar{E}(\mu_0) \approx \sum_k \left(\sum_i a_{ki} \chi_i(\mu_0) \right) E(\mu_k) + \left(\sum_i b_{ki} \chi_i'(\mu_0) \right) E'(\mu_k), \tag{11}$$

showing that the correction to $E(\mu_0)$, $\bar{E}(\mu_0)$ is estimated as a linear combination of $E(\mu_k)$ and/or $E'(\mu_k)$, with coefficients determined by the choice of χ_i and μ_k.

The equation

$$\bar{E}(\mu_0) = -\int_{\mu_0}^{\infty} \bar{E}' d\mu \tag{12}$$

can also be used. It appears under different names in the literature, e.g., adiabatic connection (AC), when related to the density functional theory (DFT), or as integrated Hellmann-Feynman formula.[2] The numerical integration rule is defined by choosing ω_k and μ_k to satisfy

$$\int_{\mu_0}^{\infty} \chi_i'(\mu) d\mu = \sum_k \omega_k \chi_i'(\mu_k), \tag{13}$$

(ω_k and μ_k depend on μ_0). For these ω_k, μ_k, we have, using Eqs. (8) and (13),

$$\begin{aligned} \int_{\mu_0}^{\infty} \tilde{E}'(\mu) &= \int_{\mu_0}^{\infty} \sum_i c_i \chi_i'(\mu) d\mu \\ &= \sum_i c_i \sum_k \omega_k \chi_i'(\mu_k) \\ &= \sum_k \omega_k \tilde{E}'(\mu_k). \end{aligned} \tag{14}$$

Using Eqs. (6) and (12), we have the quadrature formula

$$\bar{E}(\mu_0) \approx \sum_k \omega_k \, E'(\mu_k) \tag{15}$$

with ω_k and μ_k determined by Eq. (13).

C. Extrapolation formulas

For the Hamiltonians $H(\mu)$ chosen below, $E(\mu)$ behaves, for large μ, like μ^{-2}. A simple choice for the approximation basis in Eq. (7) is thus $\mu^{-2}, \mu^{-3}, \ldots$, although it is certainly not valid for small μ and more sophisticated alternatives are available.

We will now seek for the correction to $E(\mu_0)$, $\bar{E}(\mu_0)$. If the only additional information is $E'(\mu_0)$, one coefficient of the expansion (7) can be determined from Eq. (8). By using Eq. (6),

$$\bar{E}(\mu_0) \approx -E'(\mu_0)\chi_1(\mu_0)/\chi_1'(\mu_0). \tag{16}$$

Please notice that this formula, an extension of the trapezoidal rule, is also obtained for a single basis function and when μ_0 is the point imposed for quadrature [cf., Eq. (13)]. Below, this will be called the "endpoint quadrature".

In particular, for $\chi_1 = \mu^{-2}$, we have

$$\bar{E}(\mu_0) \approx \tilde{E}_1(\mu_0) = \frac{1}{2}\mu_0 E'(\mu_0). \tag{17}$$

If $E(\mu_1)$ and $E'(\mu_1)$ are also known, one can treat exactly a linear combination of three basis functions. We will choose them to be μ^{-2}, μ^{-3}, μ^{-4}. To obtain Eq. (11), we use $E(\mu_1) - E(\mu_0)$, $E'(\mu_0)$, and $E'(\mu_1)$:

$$\begin{aligned}\bar{E}(\mu_0) \approx \tilde{E}_2(\mu_0) = (E(\mu_1) - E(\mu_0)) &\frac{\mu_1^3(\mu_1 - 2\mu_0)}{(\mu_0 + \mu_1)(\mu_1 - \mu_0)^3} \\ + E'(\mu_0) &\frac{\mu_0^4}{2(\mu_0 + \mu_1)(\mu_1 - \mu_0)^2} \\ + E'(\mu_1) &\frac{\mu_1^4}{2(\mu_0 + \mu_1)(\mu_1 - \mu_0)^2}. \end{aligned} \tag{18}$$

We will call here this last approximation the "arbitrary two-point interpolation".

For the same set of χ_i, one can choose to use the E' at integration endpoint, μ_0, and find from Eq. (13) another integration point, μ_1, as well as the integration weights ω_0 and ω_1. This yields a Radau quadrature formula:

$$\bar{E}(\mu_0) \approx \tilde{E}_R(\mu_0) = \frac{1}{6}\mu_0 E'(\mu_0) + \frac{8}{3}\mu_0 E'(2\mu_0). \tag{19}$$

The formula above can be also obtained from the arbitrary two-point interpolation formula, Eq. (18), by choosing μ_1 to eliminate the term containing $E(\mu_1) - E(\mu_0)$.

D. Comparison to density functional methods

In density functional theory, $\bar{E}$ is obtained from a functional of the density. The adiabatic connection, Eq. (12), is used in the Kohn-Sham approach[3] of DFT both to interpret it[4–7] and to produce DFAs (see, e.g., the use of model holes,[8] of hybrid methods,[9] or its connection to scaling relationships[10]). In this context, the model energy to be corrected, $E(\mu_0)$, is that of the Kohn-Sham system. We will choose below to use Hamiltonians appearing in a generalization of the Kohn-Sham approach,[1,11] where μ_0 can be chosen to allow for various long-range interaction between electrons, providing a family of Hamiltonians, $H(\mu_0)$.

The essential difference between EE and DFAs, even when using the same $H(\mu)$, comes from Eqs. (5) and (6) not being satisfied when $\bar{E}(\mu)$ [and/or $\bar{E}'(\mu)$] is given by a DFA, even when $E(\mu)$ and $E'(\mu)$ can be obtained accurately for the model systems. Thus, in the limit of exact integration along the AC, Eq. (12), with $\bar{E}'$ given by a DFA, one obtains just what the DFA provides, while with EE, Eqs. (5) and (6) can be used, and the physical energy is obtained accurately. Stated differently, in EE we let the model systems decide what the correct coefficients c_i should be in Eq. (7), while in DFAs we transfer the correction from some model and hope that it will be accurate. We should underline, however, that in DFAs one usually considers more complicated forms for the χ_i than the ones which were given above.

A further difference to DFAs is that the EE is not restricted to ground states.

Please notice that in this paper, $\bar{E}$ is not further partitioned into further terms, as it is done in the Kohn-Sham approach. When such a partition is made, special attention has to be given to size-consistency issues which can be more complicated for energy components than for the total energy (see, e.g., Ref. 12).

E. Model Hamiltonians

In this paper we will consider model Hamiltonians of the form

$$\begin{aligned} T(\mu) &= T, \\ W(\mu) &= \sum_{i<j} \mathrm{erf}(\mu r_{ij})/r_{ij}, \\ V(\mu) &= \sum_i v_{ne}(r_i) + v_{hxc}(r_i;\mu), \end{aligned} \tag{20}$$

where T is the operator for the kinetic energy, r_i are the positions of the particles, $r_{ij} \equiv |r_i - r_j|$, v_{ne} is the physical external potential, v_{hxc} is the Hartree, exchange, and correlation potential in the LDA), in which there is a μ-dependence, μ-LDA.[11,13,14] The choice of $V(\mu)$ and $W(\mu)$ is motivated by the intention to have a direct comparison to the range-separated DFA (see, e.g., Ref. 11). For the latter, both accurate and approximate calculations are available.[15–17] In contrast to standard Kohn-Sham calculations, μ-LDA works almost as well as the gradient corrected approximations. Good results were obtained for valence electrons as long as μ was not chosen too small (larger than ∼1/2 to 1 bohr^{-1}, see, e.g., Refs. 11, 18, and 19).

To produce $V(\mu)$, the μ-LDA functional was used in its spin-unpolarized form (and not in the local spin-density approximation, μ-LSDA, where spin-polarization is taken into account) in order to avoid size-consistency problems, see, e.g., Refs. 11, 20, 21, and 22. Although size-consistency problems may show up in the LDA (see, e.g., Ref. 11), they are related to degeneracy issues which do not show up in the examples discussed below.

For the choice of Hamiltonian made above, Eq. (20), $\bar{E} \propto \mu^{-2}$ for large μ.[13,15,16,23] This is essentially a dimensional argument.

F. Technical details

For the choice of $H(\mu)$ made above, $E(\mu)$ can be directly extracted from the output of the range-separated configuration interaction program of the MOLPRO code.[18,24–32] Because $E'(\mu)$ is not immediately available from the present version of MOLPRO, a numerically inefficient, but convenient scheme was used: a dense list of $E(\mu)$ was generated and was followed by spline interpolation and differentiation.[33] Some numerical noise can be noticed in some of the figures. It is due to the numerical grid used in the density functional calculation part, present when calculating $E(\mu)$ through $V(\mu)$, which is further amplified by the numerical differentiation. As this noise is of no relevance for the present study, no effort was made to eliminate it.

The cc-pV5Z basis sets were used, except for H$^-$ and the first excited $^1\Sigma_g^+$ state of H_2 (having a strong $H^+ \ldots H^- \leftrightarrow H^- \ldots H^+$ character) where the aug-cc-pV5Z was used.[34–37] These basis sets should allow chemical accuracy (≈1 kcal/mol) for $E(\mu)$ for all the systems presented in this paper. This assumption was checked against more reliable data, e.g., Ref. 38 for the hydrogen molecule in its ground state and first excited triplet state, and Ref. 39 for the $E, F^1\Sigma_g^+$ state.

For the Be atom, a pseudopotential[40] was used to stay with two-electron systems, and thus simplified the treatment of correlation.

The correlation is obtained for the two-electron systems at the level of a full configuration interaction calculation. For the uniform electron gas, correlation energies are available from a parametrization of quantum Monte Carlo data.[14]

The error of the approximation due to numerical integration is given by

$$\Delta\bar{E}(\mu_0) = \tilde{E}(\mu_0) - \bar{E}(\mu_0), \tag{21}$$

where $\tilde{E}$ is obtained by the numerical methods described above. The values of $\bar{E}(\mu)$, which are considered accurate, and are taken as a reference are given by Eq. (4), using the results obtained in the basis sets given above.

III. NUMERICAL RESULTS

A. General behavior

As EEs are constructed to vanish when μ_0 approaches infinity (an exact condition), and as the approximations were constructed using the expansion for large μ [Eqs. (17)–(19)], we will study below the behavior at intermediate μ_0. The approximations worsen significantly for small μ_0; in the limit of $\mu_0 = 0$, they even vanish: $\tilde{E}(\mu_0 = 0) = 0$.

When the large μ regime is abandoned, by lowering μ_0, there is a critical value of μ_0 for which the absolute error, $|\Delta\bar{E}(\mu_0)|$ becomes larger than chemical accuracy (1 kcal/mol). We call this the "smallest acceptable" μ_0. As oscillations can occur in $\Delta\bar{E}(\mu_0)$, further lowering μ_0 may bring back errors below 1 kcal/mol, but this situation is considered to be accidental, and is not discussed.

The ground state of the uniform electron gas is a good test case for the quadrature formulas, as for it μ-LDA is exact by construction.

In Fig. 1 (top, left), one can follow the error $\Delta\bar{E}$ as a function of μ_0 for the uniform electron gas with the density given by $r_s = 2$. This value of r_s was chosen as a typical valence density (see, e.g., Ref. 41). The endpoint extrapolation [$\tilde{E}_1$, Eq. (17), dashed curve in Fig. 1, top, left] shows the expected behavior: small error when μ_0 is large, but large when μ_0 is small. The behavior at small μ_0 is important, however, as models are expected to be less expensive to calculate when μ_0 is small, and from the experience with μ-LDA calculations we would like to have μ_0 less than ≈1.

B. Systematic improvement

With EE one has the possibility to increase the accuracy by adding information from new models. In the example above, when $\tilde{E}_R$, the Radau quadrature, is used

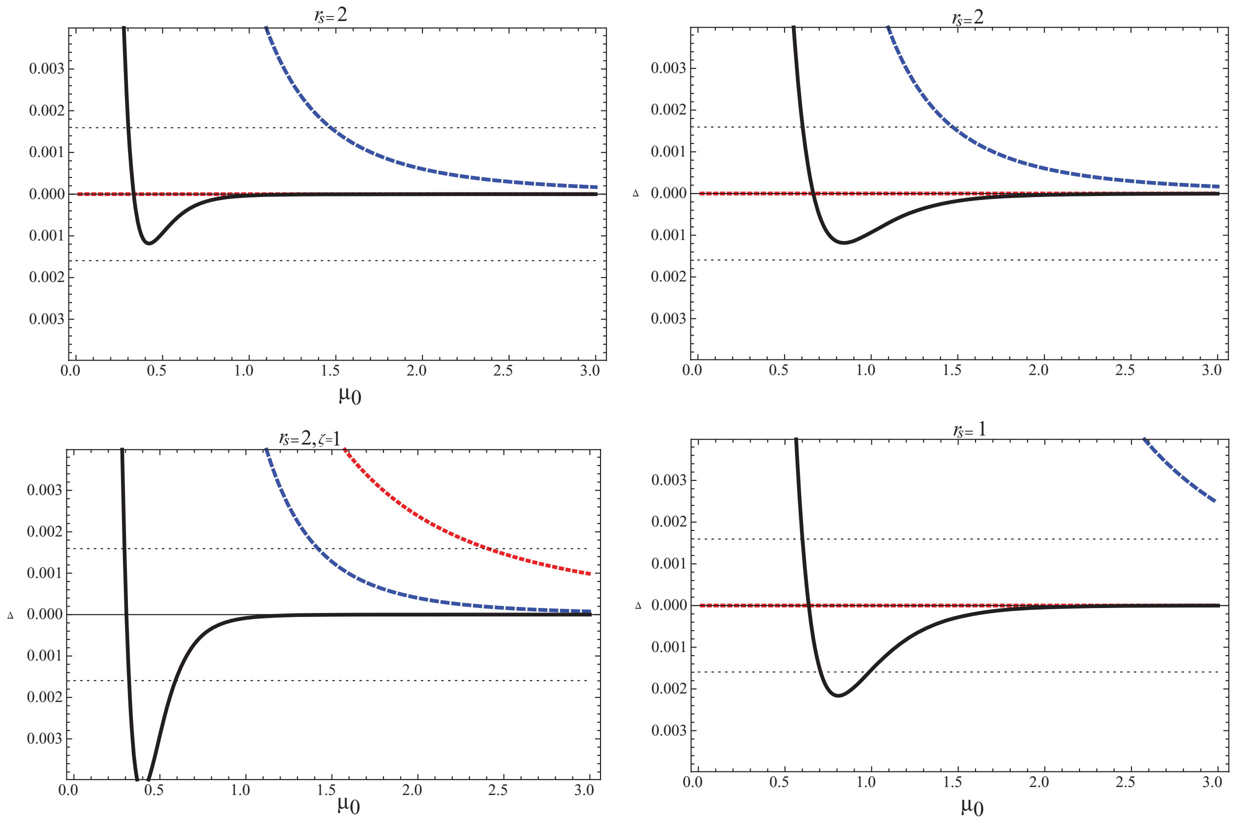

FIG. 1. The error of the numerical integration, $\Delta\bar{E}$, in the uniform electron gas using the endpoint quadrature, $\tilde{E}_1$, Eq. (17), dashed curve; two-point Radau quadrature, $\tilde{E}_R$, Eq. (19), full curve; compared to the spin-unpolarized μ-LDA energy correction, dotted curve. The horizontal thin dotted lines mark chemical accuracy (±1 kcal/mol). The panels correspond to: $r_s = 2$, spin-unpolarized, as a function of μ_0 (top left); $r_s = 2$, spin-unpolarized, as a function of $\mu_>$ (top right); $r_s = 2$, fully spin polarized, as a function of μ_0 (bottom left); $r_s = 1$, spin-unpolarized, as a function of μ_0.

(an additional point at $\mu_1 = 2\mu_0$), Eq. (19), the "smallest acceptable" μ_0 decreases from ≈ 1.5 for the endpoint quadrature ($\tilde{E}_1$) to ≈ 0.3 for the Radau quadrature ($\tilde{E}_R$). This exemplifies how a systematic improvement is possible by choosing a better numerical approximation. However, this improvement has been payed by the need of a new model calculation for a larger μ, and the comparison may be considered biased, because calculations at larger μ could be considered more expensive. It will be assumed that the reader can easily keep this in mind when looking at the graphs and this effect will be solely illustrated for the uniform electron gas with $r_s = 2$ (see Fig. 1, top, right). There, the abscissa is not μ_0, like in most of the graphs of this paper, but $\mu_>$, the largest of the μ_k used in the quadrature [$\mu_> = \mu_0$ for the endpoint quadrature, $\tilde{E}_1$, Eq. (17), and $\mu_> = \mu_1$ for the Radau quadrature, $\tilde{E}_R$, Eq. (19)]. The figure shows that adding a quadrature point lowers the "smallest acceptable" $\mu_>$, from ≈ 1.4 to ≈ 0.6

Of course, this conclusion cannot be generalized: it can happen that the "smallest acceptable" μ_0 of the endpoint quadrature is smaller than the "smallest acceptable" μ_1 of the Radau quadrature. Although one rightfully expects that in the limit of a large number of μ_k, $\bar{E}(\mu_0)$ becomes correct, the largest μ_k is displaced to larger and larger values. Thus, improvement may be connected to a larger price to pay, not only in the number of calculations, but also in the price of individual model calculations which are considered to become more expensive as the model system approaches the physical one.

C. Arbitrary two-point interpolation

With numerical integration of Gaussian type, the number of basis functions in Eq. (7) can be twice as large as that used in Eq. (11) with the same number of reference values. The price to pay is that the μ_k cannot be chosen freely. The need to input a smaller number of model system data with Gaussian quadrature is not necessarily an economy in computing time: often the $E'(\mu_k)$ are obtained only after the $E(\mu_k)$ are known anyhow. The latter are left aside for the quadrature scheme, while they can be used in the interpolation formulas for arbitrary μ_k, e.g., in Eq. (18). Figure 2 shows the domain of μ_0 and μ_1 for which the error done by using the two-point extrapolation formula of Eq. (18) is smaller than chemical accuracy. Also shown is the line $\mu_1 = 2\mu_0$ along which Radau quadrature, Eq. (19), is performed. One can see that using $\tilde{E}_R$, the Radau quadrature formula, a quite good choice for μ_0 and μ_1 is made, in the sense that it can provide a low value for the "smallest acceptable" μ. However, one can see that it is not the best choice. One could choose μ_1 very close to μ_0 and further lower the value of the "smallest acceptable" μ still staying within chemical accuracy. However, using $\mu_1 \approx \mu_0$ needs a careful avoidance of numerical errors or the use of higher derivatives. For the sake of keeping the presentation more accessible, we will discuss below only the results obtained by endpoint and Radau quadrature.

D. Spin dependence

By the choice made above, no spin-dependence was considered for constructing $V(\mu)$. Usually this considerably worsens results with DFAs. This can be seen, e.g., for the fully spin-polarized electron gas at $r_s = 2$ (Fig. 1, bottom, left). While for a spin-polarized electron gas μ-LSDA has no error, the spin-unpolarized μ-LDA yields ≈ 2.4 for the "smallest acceptable" μ_0. The endpoint and the Radau quadratures yield better values for the "smallest acceptable" μ_0, ≈ 1.4 and ≈ 0.6, respectively. This can be connected to the behavior of $\bar{E}(\mu)$ for large μ: it decays as μ^{-2} both for the unpolarized and the fully polarized electron gas, but with different prefactors. The inclusion of the accurate $E'(\mu)$ in the quadrature formulas provides the necessary correction at large μ_0.

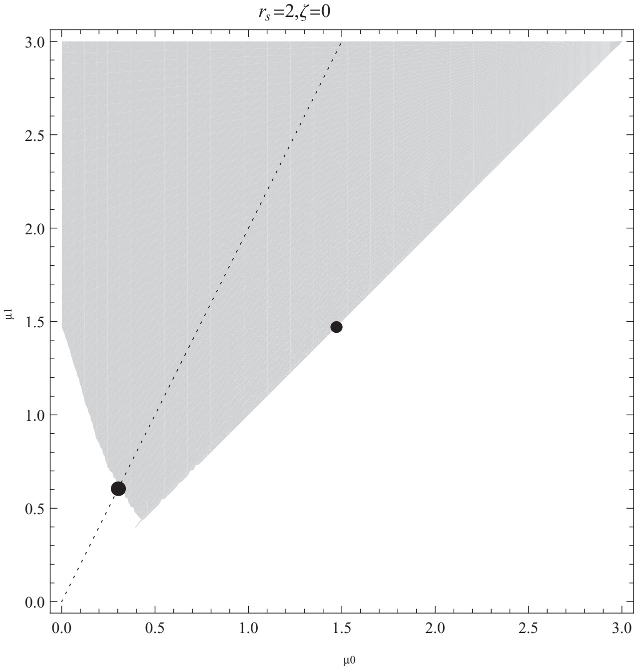

FIG. 2. The domain of μ_0 and μ_1 where the error produced by two-point extrapolation, $\tilde{E}_2$, Eq. (18), is smaller than chemical accuracy (±1 kcal/mol) is shown as the shaded area. The dots mark the "smallest acceptable" μ for the endpoint quadrature, $\tilde{E}_1$, Eq. (17), and the Radau quadrature, $\tilde{E}_R$, Eq. (19). The pairs μ_0, μ_1 of the Radau quadrature lie on the dotted line. As $\mu_1 > \mu_0$, only the upper left part of the plot is relevant.

A further example is given by the hydrogen atom (Fig. 3). When μ-LDA in its spin-unpolarized variant is used, the chemical accuracy is reached only at large values of $\mu_0 \approx 2.9$. In its spin-polarized form, however, μ-LSDA works up to $\mu_0 \approx 0.5$. Using EE [and thus the correct $E'(\mu)$] allows reaching about the same "smallest acceptable" μ_0 when using μ-LSDA.

E. System dependence

In Fig. 4 we compare the different approximations for the He atom, H_2 molecule, H^- ion, and Be atom (the latter with a pseudopotential). The approximations based upon numerical integration show a behavior similar to that observed in the uniform electron gas: a small error at large μ_0, and a breakdown at smaller μ_0. As for the gas, adding a quadrature point [as in Eq. (19)] improves the result at μ_0, although one notices that for the hydrogen molecule, the "best available" $\mu_1 = 2\mu_0$

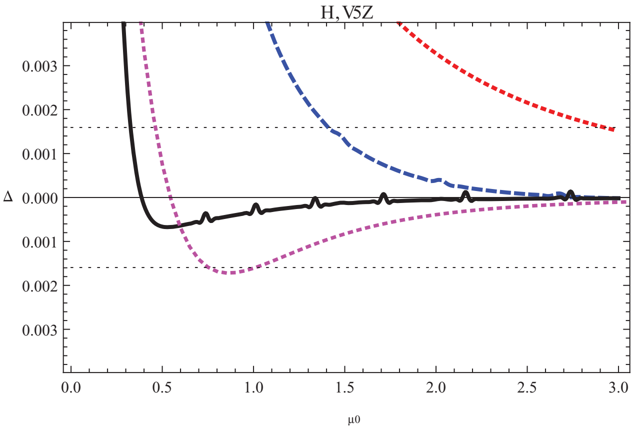

FIG. 3. Error of the numerical integration, $\Delta \bar{E}$, Eq. (21), as a function of μ_0, in hartree atomic units, for the hydrogen atom; obtained with spin-unpolarized μ-LDA (in the upper right corner, dotted curve), compared to that obtained with endpoint quadrature, $\tilde{E}_1$, Eq. (17), dashed curve, or two-point Radau quadrature, $\tilde{E}_R$, Eq. (19), full curve. The horizontal thin dotted lines mark chemical accuracy (±1 kcal/mol). Also shown, as a dotted curve staying within chemical accuracy for μ_0 larger than ≈0.5 is μ-LDA with spin polarization.

is close to the "best available" μ_0 of the endpoint quadrature [Eq. (17)].

For these systems, μ-LDA is not exact (in contrast to the uniform electron gas above). The error is small for large μ, confirming that μ-LDA is a good approximation for a short range. At smaller μ_0, however, the errors are less systematic, oscillations occur. Thus, we notice that for He and the ground state of the hydrogen molecule, at equilibrium distance, the quality of μ-LDA and EE is comparable. However, for H^-, μ-LDA worsens, and EE is clearly superior for the Be atom.

The difference between the μ-LDA and the EE results can be rationalized. As already discussed, EE is expected to work accurately in the limit of large μ, but (with the choice of χ_i made) cannot be expected to work for small μ. μ-LDA also vanishes for $\mu \to \infty$ and is expected to work quite well for large μ, but will not become exact, in general, as EE does. In contrast to EE, μ-LDA automatically uses the correct $E'(\mu = 0)$, because the leading term of the expansion around $\mu = 0$ is solely determined by the correct normalization of the pair function which is transferred from the uniform electron gas.[13,15,16] However, the next terms of the expansion of the derivative of $\partial_\mu E(\mu)$ around $\mu = 0$ are wrong in μ-LDA.[16] Thus, μ-LDA connects wrongly to the intermediate μ regime, by using features of the uniform electron gas not present in atoms or molecules.

A critical feature of μ-LDA (Refs. 1, 18, and 42) that is not avoided by the formulas for EE given above is the system-dependence of the "smallest acceptable" μ_0. It is relatively important, and is related to the significance of the parameter μ we are considering in Eq. (20) which is the inverse of a "range of interaction". For the same range of interaction, the energetic contributions are more important when the electrons are "dense". For example, in a uniform electron gas, the ratio $E(\mu)/E(\infty)$ depends on the density of the gas. Thus, if a system is "denser", the "smallest acceptable" μ_0 should increase. This feature can be seen in Fig. 1, bottom, right,

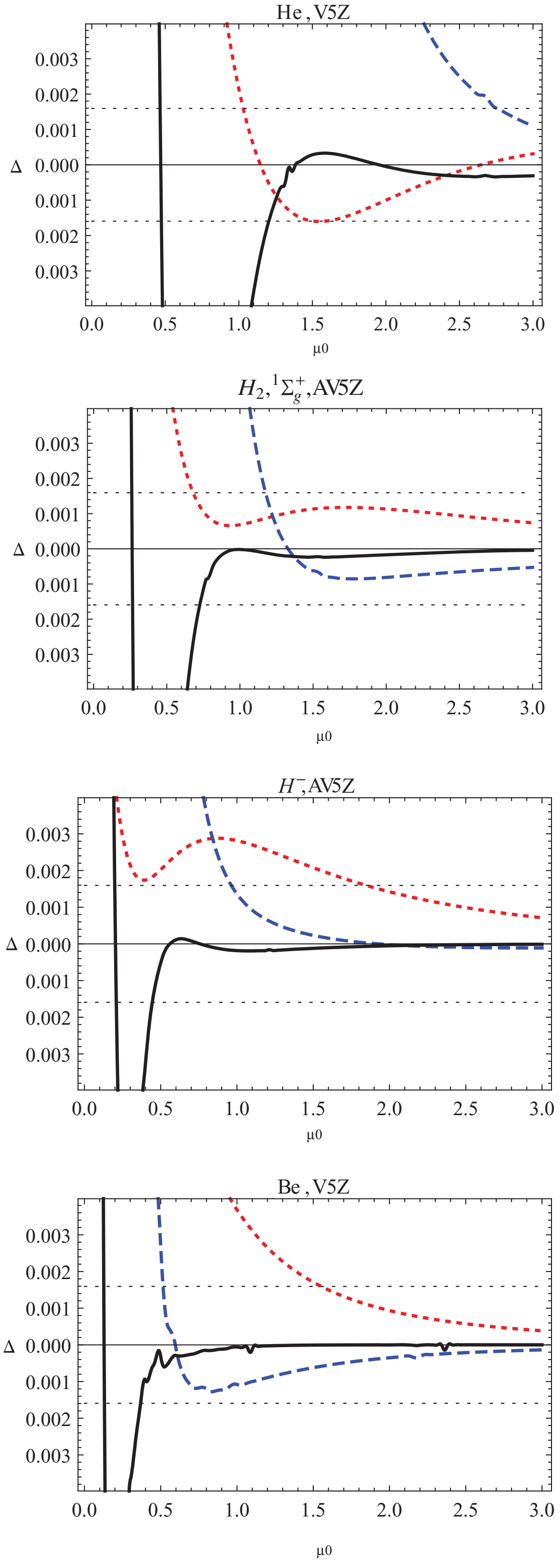

FIG. 4. Error of the numerical integration, $\Delta \bar{E}$, Eq. (21), as a function of μ_0, in hartree atomic units, compared to that of μ-LDA, dotted: for endpoint quadrature, $\tilde{E}_1$, Eq. (17), dashed, and two-point Radau, $\tilde{E}_R$, Eq. (19), full. The horizontal thin dotted lines mark chemical accuracy (±1 kcal/mol). The panels correspond to He, H_2 at equilibrium distance, H^-, and Be, from top to bottom.

presenting the errors for a uniform electron gas at a higher density ($r_s = 1$) than that used previously ($r_s = 2$, Fig. 1, top, left). It also shows up in atomic or molecular systems. For example, EE works better for the H^- ion than for the He atom (cf., Fig. 4).

F. Size-consistency

One of the advantages of using for extrapolation expressions which are linear in $E(\mu_k)$ and $E'(\mu_k)$ is that size-consistency can be preserved, i.e., that the energy of the system formed by two subsystems, A and B, infinitely far apart, is the sum of the energies of the systems A and B computed separately.

As an example, we consider the hydrogen molecule at large internuclear separations. For the (singlet) ground state, there is no physical spin polarization. In a DFA where dependence on spin-polarization is added, one necessarily obtains a different result for the dissociated hydrogen molecule, where no spin polarization is present, and for two hydrogen atoms which are fully spin-polarized, even when the densities are the same in the two calculations. This problem is usually circumvented by introducing some fictitious spin-polarization in approximate Kohn-Sham calculations for the dissociation of the hydrogen molecule.

EE was constructed to be size-consistent. Thus, as the separation between the two H nuclei increases, the error evolves from that shown for the equilibrium distance in Fig. 4, second panel from the top, to the one where the errors are twice as those shown for the H atom, Fig. 3. There is no need to artificially introduce spin-polarization for EE to describe correctly the H_2 molecule.

G. Excited states

As the model Hamiltonians can be constructed to have the same symmetry as the physical Hamiltonian, states can be identified, and symmetry-related degeneracies can be kept. Of course, there is no guarantee that the energetic ordering of the states is correct, but states can be followed as μ changes.

The lowest triplet excited state comes out well both in spin-polarized μ-LDA and with EE. However, if spin-polarization is not taken into account, μ-LDA does not work so well, while EE is little affected (see above the discussion about spin polarization), as can be seen in Fig. 3 for the hydrogen atom errors (which are half the errors at the dissociation of the hydrogen molecule in the lowest triplet state).

More difficult than the excited triplet state is the case where the excited state has the same symmetry as the ground state. For example, the $E, F\,{}^1\Sigma_g^+$ excited state of the hydrogen molecule has a strong ionic resonant character.[43] Usually, it is argued that DFAs work better than Hartree-Fock, as the exchange-correlation hole is more strongly localized than the exchange hole (see, e.g., Refs. 44 and 45). This is essentially valid for ground states. When $H^+ \ldots H^- \leftrightarrow H^- \ldots H^+$ dominates, as in the case of the $E, F\,{}^1\Sigma_g^+$ state,[43] the opposite is true: the exchange-correlation hole is less localized than in Hartree-Fock. Thus, μ-LDA is not expected to give good results, and introducing spin-polarization does not help. However, when using EE no significant difference is noticed between the errors for the excited singlet, Fig. 5, and those for the ground state of the hydrogen molecule, Fig. 4.

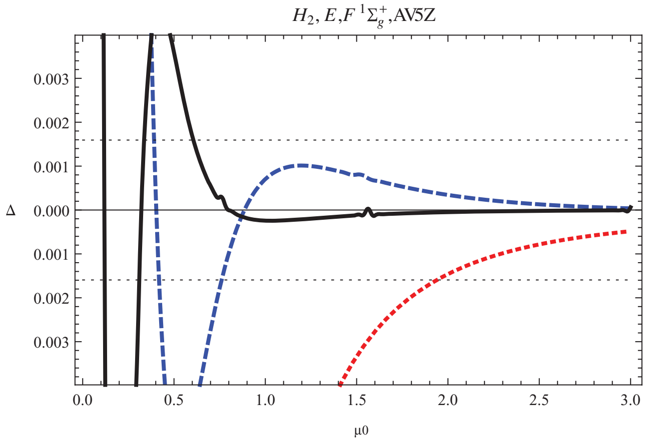

FIG. 5. Error of the numerical integration, $\Delta\bar{E}$, Eq. (21), as a function of μ_0, in hartree atomic units, compared to that of μ-LDA, dotted: for endpoint quadrature, $\tilde{E}_1$, Eq. (17), dashed, and two-point Radau quadrature, $\tilde{E}_R$, Eq. (19), full. For the $E, F\,{}^1\Sigma_g^+$ state of the H_2 molecule $R = 4.2$ bohr. The horizontal thin dotted lines mark chemical accuracy (±1 kcal/mol).

H. Energy differences

Up to now, only total energies were analyzed. The nearly uniform quality of EE (sometimes related to size-consistency) often allows for a better description of energy differences than μ-LDA, like excitation energies, or potential energy surfaces, in particular, when μ-LDA describes well only one of the terms of the difference considered. For example, as the excited triplet state of the hydrogen molecule is better described by EE than by spin-unpolarized μ-LDA, but with a similar quality for its ground state, the excitation energy will be better described by EE than by μ-LDA.

Errors in energy differences can sometimes take advantage from error compensation. For EE, the effect is expected to be less important than for μ-LDA, as the quality worsens quickly when the basis of χ_i used in defining the approximation starts to fail. For example, the "smallest acceptable" μ_0 for the electron affinity of the hydrogen atom is ≈2.2 with spin-unpolarized μ-LDA; for the H atom (the worse of H and H^-) it is ≈2.9. For the same energy difference, the endpoint quadrature yields the "smallest acceptable" μ_0 which is only smaller by 0.1 than the worse of H and H^-. The effect is even smaller for the Radau quadrature.

I. Analogies

The method discussed in the present paper presents some analogy to existing procedures. EE can be seen as a variant of perturbation theory. Perturbation theory produces the energy of the physical Hamiltonian by perturbing a model Hamiltonian. The perturbation is multiplied by a parameter that allows the construction of the eigenvalues of the perturbed Hamiltonian by using power series. The energy and its derivatives are typically evaluated at the value of the parameter characterizing the model system, to extrapolate the value of the energy for the value of the parameter characterizing the physical system. The present paper considers, for the same aim, (i) functional dependencies different than that of a polynomial, and (ii) the use of multiple values for the parameter, by using well-known extrapolation techniques. Point (ii) above also occurs in methods such as first-order perturbation iteration method,[46] where the perturbation is redefined in the process of approaching the physical system.

Other examples are extrapolations to the full configuration interaction limit (see, e.g., Ref. 47), or to the complete basis set limit (see, e.g., Ref. 48) where the asymptotic behavior is also used (see, e.g., Refs. 49 and 50). The analogy to the complete basis set extrapolation of Ref. 51 goes even further, as in the latter, one imposes that different type of calculations lead to the same extrapolated value.

EE does not require $V(\mu)$ to be produced by the derivative of some functional with respect to the density. One is free, however, to choose such a $V(\mu)$. In this case, and when Eq. (12) is used, an analogy with the AC of DFT exists. To follow the latter, however, the Schrödinger equation of the physical system has to be accurately solved, because it requires the knowledge of the exact density.[4,5] Calculations along the AC of DFT can be accurately done, but they are significantly more expensive than solving the Schrödinger equation for H alone, as they have to be repeated for several Hamiltonians, for different $H(\mu)$.[17,52–56] EE with quadrature formulas should be rather seen as a numerical approximation to a Hamiltonian-driven AC.[57]

Naturally, a connection exists with the techniques using the AC for constructing hybrid functionals, as given, e.g., by Becke for the half-and-half method,[9] or to interpolations between the situation when the interaction between electrons is vanishingly small (second-order perturbation theory) and when it becomes infinitely strong (strictly correlated electrons).[58,59] In this paper, however, no attempt was made about to construct a DFA.

There is also some similitude with the technique proposed by van Leeuwen and Baerends[60] to extract the exact energy from a series of densities by finding the corresponding Kohn-Sham potential for each of them. EE, however, does not require the knowledge of the exact density, nor the solution of an inverse problem.

Finally, the EE presented in this paper can be seen as an extension of the methods presented in Refs. 61 and 62 where extrapolation was used in connection with non-local one-particle operators.

IV. CONCLUSIONS AND PERSPECTIVES

The approach presented in this paper uses model Hamiltonians (characterized by a parameter, μ), to produce energies which are extrapolated to the physical one using standard numerical techniques. For good quality results, the energy of the model systems should be obtained accurately, and knowledge about the way the model energies extrapolate to the physical systems is important.

The numerical techniques to estimate the exact energy use as an input the difference between the energies of two different models and/or the derivative of the model energy with respect to the parameter transforming the models into the physical system. This kind of information is not used when constructing density functional approximations, and is one of the keys of the improvements seen in this paper.

Most of the results of the paper were produced using the approximations $\tilde{E}_1$, Eq. (17), and $\tilde{E}_R$, Eq. (19).

As one can choose the model Hamiltonian to have the same symmetries as the physical one, states can be identified and followed.

Excited states can be treated on the same footing as the ground state.

EE does not show inherent size-consistency problems. Size-consistency can be satisfied when size-consistent methods are used to solve the Schrödinger equations for the model systems.

The approach was found to work quite well for small two-electron systems and for the uniform electron gas.

A surprisingly small number of models is needed to produce an accuracy comparable, or even better than that of range-separated hybrid density functional approximations. A small number of quadrature points was noticed also in previous work for adiabatic connections.[63]

One can hope that the effort can be reduced by a judicious choice of the model system, e.g., by elimination of the electron-electron cusp, as for the Hamiltonian studied in this paper, or by reducing the space of virtual orbitals, as in Ref. 62.

There are many issues left open for exploration.

The applicability of EE, as presented in this paper will depend on the effort needed to obtain accurate solutions for the Schrödinger equation for the model systems. This aspect was not studied in the paper.

For the present paper, only very small systems were considered, for which the error made by numerical integration can be directly analyzed by comparison with accurate results. No attempt was yet made to use error estimates associated to the quadrature rules given above. Furthermore, error propagation was not studied in this paper. Here are two simple examples for error propagation. From a calculation with a very weak interaction, for a non-degenerate system, one might guess that a single Slater determinant is enough. However, when staying with the latter, the best extrapolation will yield the Hartree-Fock result, not the exact one. The same type of error shows up if one scales linearly the electron-electron interaction, and computes the energy only to second order. Extrapolation to full interaction does not yield more than the full second-order energy. This does not mean that error propagation will always be present. Consider, e.g., the stretched H_2 molecule. In this case, some repulsive interaction produces the correct ground state,[64] and any expectation value such as $\langle \partial_\mu H \rangle$ is correct. One can thus expect to get correct estimates for E'. Please notice that with the Hamiltonian used here, Eq. (20), $\partial_\mu W$ is short-ranged and thus $\langle \partial_\mu W \rangle$ can be produced with order N algorithms.

Other forms of model Hamiltonians $H(\mu)$ may be more appropriate. A totally different form was already mentioned above (selection of the virtual space, Ref. 62). To stay with the same form of $H(\mu)$, one may choose $V(\mu)$ different from the type explored in this paper where it was chosen to be derived from a DFA. Even when DFAs are used, $V(\mu)$ does not have to be a functional derivative. In the density functional papers, potentials have been proposed which yield good results for certain properties (not the ground state energy), without being constructed as functional derivatives (see, e.g., Ref. 65). Other forms for $V(\mu)$ could be chosen as well, e.g., of the optimized effective potential type (see, e.g., Refs. 66–68), or even with no reference to density functional theory. EE can provide energies also for such potentials. For example, taking $V = V_{ne}$ produces a similar quality of results for the atoms and molecules considered in this paper.[69]

The differentiability of $E(\mu)$ was used in this paper. However, it is possible to use only conditions given in Eq. (5). The parameter μ does not even have to be a continuous variable. For example, it can be an orbital index.[62]

Furthermore, other numerical techniques to obtain approximations to $\bar{E}(\mu)$ should be envisaged, in particular, in order to reduce the system dependence which is still too important (cf., the system dependence of the "smallest acceptable" μ_0 in Fig. 4).

Properties could be computed by EE by using the Hellmann-Feynman theorem.

Although no functional of the density has to be given, the importance of using a correct E' is a hint for further improvement of DFAs. For example, the energy extrapolation underlines the advantage of using the correct E' and not that provided by the DFA. DFAs might contain a parameter which is adjusted to obtain the correct E'. Similarly, one could compute energies for different values of μ, and impose that the difference in the approximate density functionals accurately corrects for such a change. An improvement achieved this way can be found in Ref. 62. Such a parameter can be seen as one of the possible ways to define "alternative spin densities"[70–74] in DFAs, which would be needed, in particular, in multi-reference μ-LDA.[64]

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