

The limits of local correlation theory: Electronic delocalization and chemically smooth potential energy surfaces

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Local coupled-cluster theory provides an algorithm for measuring electronic correlation quickly, using only the spatial locality of localized electronic orbitals. Previously, we showed [J. Subotnik *et al.*, *J. Chem. Phys.* **125**, 074116 (2006)] that one may construct a local coupled-cluster singles-doubles theory which (i) yields smooth potential energy surfaces and (ii) achieves near linear scaling. That theory selected which orbitals to correlate based only on the distances between the centers of different, localized orbitals, and the approximate potential energy surfaces were characterized as smooth using only visual identification. This paper now extends our previous algorithm in three important ways. First, locality is now based on both the distances between the centers of orbitals as well as the spatial extent of the orbitals. We find that, by accounting for the spatial extent of a delocalized orbital, one can account for electronic correlation in systems with some electronic delocalization using fast correlation methods designed around orbital locality. Second, we now enforce locality on not just the amplitudes (which measure the exact electron-electron correlation), but also on the two-electron integrals themselves (which measure the bare electron-electron interaction). Our conclusion is that we can bump integrals as well as amplitudes, thereby gaining a tremendous increase in speed and paradoxically increasing the accuracy of our LCCSD approach. Third and finally, we now make a rigorous definition of chemical smoothness as requiring that potential energy surfaces not support artificial maxima, minima, or inflection points. By looking at first and second derivatives from finite difference techniques, we demonstrate complete chemical smoothness of our potential energy surfaces (bumping both amplitudes and integrals). These results are significant both from a theoretical and from a computationally practical point of view. © 2008 American Institute of Physics. [DOI: 10.1063/1.2821124]

I. INTRODUCTION

A. Local coupled-cluster theory: A fast method for measuring electronic correlation

Local coupled-cluster theory¹⁻⁶ is a quantum chemist's attempt to calculate the ground-state energy of molecules to a high degree of accuracy in a short amount of time. The basic idea is to enforce the locality of electronic correlation (following the original ideas of Saebo and Pulay⁷) within the context of coupled-cluster theory.⁸⁻¹¹

The coupled-cluster approach⁸⁻¹¹ towards calculating electronic correlation is to make the ansatz that the n -electron fully correlated ground state has the following form:

$$\Psi = e^{\hat{T}}\Psi_0. \quad (1)$$

Here, Ψ_0 is a single Slater determinant, often the Hartree-Fock (HF) ground state. \hat{T} is an excitation operator which

should account for electronic correlation. For the case of coupled-cluster singles and doubles (CCSD), denoting occupied orbitals ij and virtual orbitals ab , \hat{T} assumes the form $\hat{T} = \sum_{ia} t_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j$. After making the CCSD ansatz, one plugs that ansatz into the Schrödinger equation $\hat{H}\Psi = E\Psi$, and one effectively transforms the problem of electron-electron correlation into a nonlinear algebraic equation. One needs only solve for the variables t_i^a and t_{ij}^{ab} , the so-called t -amplitudes, in order to completely characterize the electronic correlations in the ground state (up to the doubles level). Unfortunately, when one works through the algebra, one finds that the CCSD algorithm scales as N^6 where N is the size of the basis set. One is forced to compute many matrix products between integrals and t -amplitudes (e.g., $\sum_{ef} t_{ij}^{ef} \langle ab || ef \rangle$), which lead to the problematic sextic scaling. The strength of the CCSD ansatz, however, is that the algorithm sums up correlations to infinite order, and calculates correlation energies more accurately than MP2 perturbation theory.¹²

Local correlation theory is a method designed to circumvent the expensive scaling which is all too common for elec-

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tronic correlation methods. In its initial formulation by Saebo and Pulay,⁷ one achieves computational savings by limiting the excitations to local excitations: $\hat{T}_{\text{local}} = \sum_{ia \text{ close}} t_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{ijab \text{ close}} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$. For ia not close together, one sets $t_i^a = 0$. By limiting the number of variables (t_i^a and t_{ij}^{ab}) to a linear number, one reduces the dimensionality of the problem so that one can more easily and quickly solve the electronic problem. Early work on local correlation by Murphy *et al.*¹³ and Reynolds *et al.*¹⁴ built upon the ideas of Saebo and Pulay by recognizing that one could exploit locality not just in limiting the number of t -amplitudes variables, but also in computing the necessary Hamiltonian matrix elements. These matrix elements are usually matrix products of two-electron integrals with other tensors, and Murphy *et al.* and Reynolds *et al.* invoked the pseudospectral approach for calculating two-electron integrals in a localized basis, achieving far larger computational savings than anyone before. Several years later, Werner and co-workers^{1,15–26} applied and updated these methods to a wide variety of electronic structure methods, including LCCSD, achieving a linear-scaling algorithm in certain regimes. According to their approach, one divides up the amplitudes into strong, moderate, weak, and very weak amplitudes, and treats the different amplitudes at different theoretical levels. By limiting the number of strong amplitudes, one can achieve enormous computational savings.

B. Mathematically smooth potential energy surfaces

Until recently, the largest drawback to the groundbreaking work of Saebo and Pulay, Schütz, Werner, and others was that their method yielded discontinuous potential energy surfaces.²⁷ By choosing which t_i^a and t_{ij}^{ab} to compute explicitly at which level, the Saebo-Pulay-Schütz-Werner algorithm chooses coordinates to describe electronic correlation which are specifically designed for one particular choice of nuclear geometry, and which cannot be readily and smoothly transferred to another choice of nuclear geometry. When the nuclear geometry changes, and the domains should change naturally as well, the Saebo-Pulay-Schütz-Werner algorithm often produces a discontinuity in the electronic energy. Russ and Crawford found these discontinuities to be on the order 1–5 mhartrees for small systems.²⁷ As such, LCCSD as traditionally formulated is not reliable for complicated, multi-dimensional geometrical optimizations nor can it be used for Born-Oppenheimer dynamics.

Recently, we showed^{28,29} that through a different formulation of the problem of local correlation, one could achieve mathematically smooth potential energy surfaces while retaining the computational savings of a linear-scaling local correlation algorithm. The solution lies in bumping the amplitudes in the amplitude equations. At its most basic level, bumping can be defined as smoothing out the transition between strong and weak amplitudes by selectively inserting a function that smoothly goes from zero to one. More precisely, the bumping procedure is defined as follows. If we plug the *full* coupled-cluster ansatz into the Schrödinger equation, we arrive at a nonlinear equation for the t -amplitudes (which are the variables to solve for) as follows:

$$\mathbf{I}(\mathbf{n}) + \mathbf{A}^{(d)}(\mathbf{n}) \cdot \mathbf{t} + \mathbf{R}(\mathbf{t}, \mathbf{I}(\mathbf{n}), \mathbf{F}(\mathbf{n})) = 0. \quad (2)$$

Here \mathbf{n} represents nuclear coordinates, \mathbf{t} represents the t -amplitudes for which we must solve, $\mathbf{I}(\mathbf{n})$ represents integrals dependent on the nuclear coordinates, $\mathbf{A}^{(d)}(\mathbf{n})$ is a diagonal matrix dependent on the nuclear coordinates, and $\mathbf{R}(\mathbf{t}, \mathbf{n})$ is a complicated expression, involving matrix products of integrals \mathbf{I} , the Fock matrix \mathbf{F} , and t -amplitudes \mathbf{t} . Bumping the amplitudes means replacing the exact expression in Eq. (2) with an approximate equation which enforces locality by modifying (i) the \mathbf{t} -term in the \mathbf{R} term and (ii) the entire \mathbf{R} -term on the outside,

$$\mathbf{I}(\mathbf{n}) + \mathbf{A}^{(d)}(\mathbf{n}) \cdot \mathbf{t} + \mathbf{G} \cdot \mathbf{R}(\mathbf{G} \cdot \mathbf{t}, \mathbf{I}(\mathbf{n}), \mathbf{F}(\mathbf{n})) = 0. \quad (3)$$

Here \mathbf{G} is a diagonal matrix made up of bump functions. To be as explicit as possible, let us restrict to the case of doubles only. In that case, the bumped equations in an orbital basis become

$$I_{ijab}(\mathbf{n}) + A_{ijab}^{(d)}(\mathbf{n}) t_{ij}^{ab} + g_{ijab} R_{ijab}(g_{klcd} t_{klcd}, \mathbf{I}(\mathbf{n}), \mathbf{F}(\mathbf{n})) = 0. \quad (4)$$

Locality is enforced by forcing g_{ijab} to equal 1 when $ijab$ are deemed close together, and equal to 0 when $ijab$ are far apart. Of course, g must go smoothly from 1 to 0. The exact form of g will be discussed in Sec. III. We define the bumped t -amplitudes by

$$\tilde{t}_{ij}^{ab} = g_{ijab} t_{ij}^{ab}. \quad (5)$$

Our approach maintains a unique, well-defined, smoothly varying localized ansatz for the coupled-cluster wave function, which is required for smooth potential energy surfaces. Effectively, the essential difference between our approach and the standard Saebo-Pulay-Schütz-Werner approach is that, in order to reduce the scaling of the LCCSD algorithm, we have smoothly modified the form of the Hamiltonian in Eq. (4) (when solving for the effects of correlation). This allows us to smoothly enforce locality of the local CC wave function, rather than enforcing locality *a priori*, which would produce the standard discontinuities.

Using this idea, mathematical smoothness of our LCCSD potential energy surfaces is guaranteed by the implicit function theorem.³⁰ From a chemical point of view, however, mathematical smoothness is not terribly useful, and we must necessarily introduce a separate notion of *chemical* smoothness, as discussed in Ref. 29.

C. Chemically smooth potential energy surfaces

Quantum chemistry algorithms search potential energy surfaces with step sizes often on the order of 0.001 Å, which is a typical nuclear displacement according to a Born-Oppenheimer dynamics algorithm with femtosecond time steps. Thus, for our LCCSD algorithm to be chemically useful, one must require that surfaces “behave smoothly,” i.e., they must not suffer wiggles, on fixed length scales of 0.001 Å. More generally, however, we will now define an approximate potential energy surface (PES) $\zeta(\mathbf{R})$ to be *chemically* smooth provided that there are no artificial points $x \in \mathbf{R}$ and tangent directions \vec{y} such that $\nabla|_x \cdot \vec{y} = 0$ or

$\nabla \nabla|_x \cdot \vec{y} = \vec{0}$. In one dimension, our definition is that ζ is chemically smooth if and only if there are no artificial maxima, minima, or inflection points: $f'(x) \neq 0$, $f''(x) \neq 0$. Here, a stationary point x on the bumped surface is artificial if the exact PES does not have a corresponding stationary point x_0 near x . In other words, a PES is not chemically smooth if, when the local approximation distorts the surface, new stationary points suddenly appear.

In our paper of 2006,²⁹ we argued that with a big enough smoothing window, our algorithm could produce chemically smooth PES's. As a demonstration, we offered pictures of the PES's that appeared smooth to the naked eye.²⁹ With our new and rigorous definition of chemical smoothness, we now compute first and second derivatives to prove definitively that chemical smoothness can indeed be achieved (and with the further approximations discussed in Sec. II). This is discussed in Sec. VI.

D. Maximizing computational efficiency and delocalized electronic orbitals

In addition to the problem of smoothness, two outstanding problems remain for an efficient LCCSD method. First, the prefactor for performing a near-linear scaling LCCSD computation is large when we include all integrals necessary to solve the standard, amplitude-bumped LCCSD equations in Eq. (2).²⁹ In this paper, we investigate how one may trim down and bump the *integrals* and intermediate tensors in our algorithm, much as the *amplitudes* were originally bumped in 2005.²⁸ We find that we can make further approximations for the integrals and intermediates, achieving even greater speed of the entire algorithm. This is discussed in Sec. II.

Second, there remains the question of how best to bump the amplitudes (and potentially the integrals) in the LCCSD amplitude equations. The Boughton-Pulay procedure³¹ used by Schütz and Werner is based on atomic orbital information and is not applicable if we insist on smooth potential energy surfaces. In the past, we have bumped the amplitude t_{ij}^{ab} according to a simplistic criterion: the distances between the centers of the orbitals $ijab$ (Ref. 29) as well as the two-electron matrix elements $(ia|ia), (ii|jj)$.²⁸ Neither one was satisfactory, as discussed in Sec. III. In this paper, we explore a new selection criterion which accounts for both the location and spatial extent of orbitals $ijab$ while maintaining computational efficiency. We find that, in so doing, one can construct a more accurate algorithm than was possible heretofore while keeping the same number of amplitudes.

II. BUMPING THE INTEGRALS

Bumping the amplitudes in the LCCSD amplitude equations is not enough to ensure a fast local algorithm for computing correlation energies. One obvious problem is that there are four terms in the amplitude equations which decay only as fast as the Coulomb repulsion decays. In the full CCSD equations, these terms look like

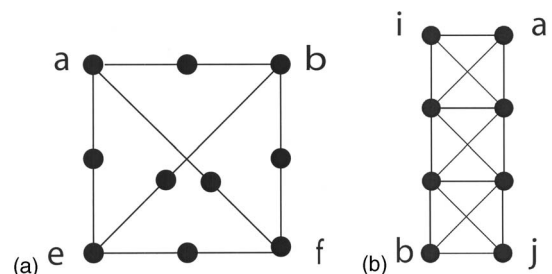


FIG. 1. (a) and (b) show just how many two-electron integrals are needed for different combinations of occupied and virtual orbitals if we do not bump the integrals. An orbital p is represented by a shaded dot, and lines connecting any orbitals p and q indicate that these two orbitals are paired together when selecting amplitudes. ij indicate occupied orbitals, and $abef$ indicate virtual orbitals. (a) The two-electron integrals necessary for the all virtual case. If we include all amplitudes up to 3 Å apart, each line segment without a dot represents a distance of 3 Å. Therefore, in going from a to b , we must include some integrals up to 6 Å apart, thus highlighting the need to bump the integrals for computational efficiency. (b) One set of necessary two-electron integrals for the half occupied, half virtual case. If we include all amplitudes up to 3 Å apart, we must include some integrals up to 9 Å apart, e.g., i to b in this diagram crosses two dots. This highlights the need to bump the integrals for computational efficiency.

$$D_q^p t_q^p + = \sum_{rs} \langle pr || qs \rangle t_s^r. \quad (6)$$

Here, we define $D_p^q = f_{pp} - f_{qq}$ and we use the “+ =” notation in the sense of C-programming, meaning that the contraction on the right-hand side is only one piece of the residual on the left-hand side. See Ref. 29, Sec. III B for more details on these terms. If we look at the term in Eq. (6) within the context of an amplitude-bumped LCCSD framework, we get

$$D_q^p t_q^p + = \sum_{rs} g_{pq} \langle pr || qs \rangle \tilde{t}_s^r. \quad (7)$$

Here, g_{pq} enforces locality of the amplitude t_p^q by going from 1 to 0 as p and q move apart. See Sec. III for more details. Even with this modified equation, however, we find that the sparsity of \tilde{t} is still not enough to limit the size of the contraction, as originally noticed by Werner and co-workers.^{1,15} Any local algorithm is forced to further approximate the LCCSD amplitude equations by bumping the integrals in four terms if one wants to construct a linear-scaling LCCSD algorithm.

A second problem is that, for all matrix multiplication products in the LCCSD amplitude-bumped equations besides the four discussed above, including all necessary terms without introducing any more approximations is still very inefficient. For example, we may consider the term as follows [in Eq. (29)]:

$$D_{ij}^{ab} t_{ij}^{ab} + = g_{ijab}^s \frac{1}{2} \sum_{ef} \hat{r}_{ij}^{ef} \langle ab || ef \rangle, \quad (8)$$

$$\hat{r}_{ij}^{ab} = \tilde{r}_{ij}^{ab} + g_{ijab}^s (t_i^a t_j^b - t_i^b t_j^a). \quad (9)$$

Again, g_{ijab}^s enforces locality of the amplitude t_{ij}^{ab} and its exact form will be given in the next section. Nevertheless, the diagram in Fig. 1(a) shows pictorially exactly how many integrals are needed to perform this matrix multiplication exactly. Here, all orbitals are represented as filled-in dots,

and a line segment between orbitals p and q means that these orbitals are selected together as amplitudes. If one selects for the amplitudes all orbitals a and b with centroids spaced less than 3 Å apart, then one must select for the integrals some orbitals whose centers are up to 6 Å apart if we want to capture the full physics of Eq. (8). According to Fig. 1(b), without further approximation, we must even include some integrals of orbitals up to 9 Å apart. Thus, even though one may construct a linear-scaling algorithm, the wall time required to construct, store, and multiply the four-center integrals becomes prohibitive.

We have now investigated the effect of bumping integrals (and intermediates) in the LCCSD equations. The general form for the twice-bumped equation is

$$\mathbf{I}(\mathbf{n}) + \mathbf{A}^{(d)}(\mathbf{n}) \cdot \mathbf{t} + \mathbf{G} \cdot \mathbf{R}(\mathbf{G} \cdot \mathbf{t}, \mathbf{G} \cdot \mathbf{I}(\mathbf{n}), \mathbf{G} \cdot \mathbf{F}(\mathbf{n})) = 0, \quad (10)$$

which should be compared to Eq. (3). Our exact prescription for integral and intermediate bumping is given in Sec. IV, but our final conclusion is that, paradoxically, bumping the integrals and intermediates always *increases* the accuracy of the LCCSD correlation energy. Whereas bumping the amplitudes empirically always leads to a correlation energy which is (in absolute value) too small, bumping the integrals leads to a stable correction, increasing the correlation energy.

III. SELECTION OF CORRELATING AMPLITUDES: THE BUBBLE METHOD

The criterion by which one decides which quartets of integrals $ijab$ to correlate together (through t_{ij}^{ab}) is the most crucial piece of any local correlation algorithm. Several options exist to choose from. For computational efficiency, one certainly wants to pick a selection criterion (via the bump function g_{ijab}) which works pairwise as follows:

$$g_{ijab} = g_{ij}^{(1)} g_{ab}^{(2)} g_{ia}^{(3)} g_{jb}^{(4)} g_{ib}^{(5)} g_{ja}^{(6)}. \quad (11)$$

In theory, one could choose up to six different criteria, but simplicity requires that we choose the fewest bump functions (and, ideally, only one). Even so, several options still exist. For instance, most obviously, one could choose to select orbital pairs (ia) by orbital exchange integral ($ia|ia$),²⁸ or the distance between centroids ($|r_i - r_a|$),²⁹ or some other similar criteria. Smoothness of the bump function requires that the criteria be smooth as well. Thus, the Boughton-Pulay criterion³¹ (which is based on the underlying AO basis structure) cannot be immediately transformed into a differentiable selection criterion which admits bumping.

In theory, selection by exchange integral is the most physical consideration.³² After all, to first order, from perturbation theory,

$$t_{ijab} = \frac{\langle ij|ab \rangle - \langle ij|ba \rangle}{f_{ii} + f_{jj} - f_{aa} - f_{bb}} \quad (12)$$

and the two-electron integrals can be estimated from the Cauchy-Schwarz inequality

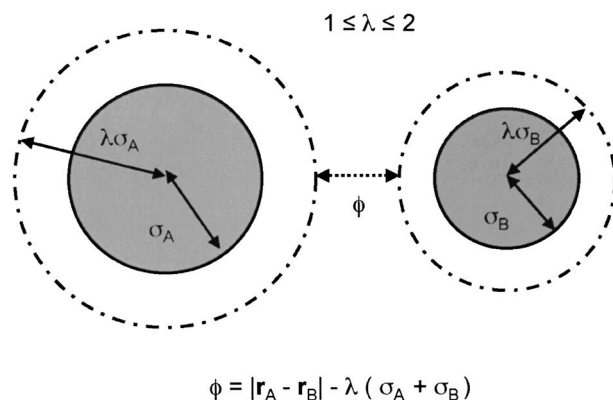


FIG. 2. The geometric meaning on the bumping variable ϕ . All data presented in this paper set $\lambda=1$.

$$|\langle ij|ab \rangle| < (ia|ia)^{1/2} (jb|jb)^{1/2}. \quad (13)$$

However, bumping by exchange integral is problematic for two reasons. First, for pairs of orbitals not strongly overlapping, the matrix element ($ia|ia$) can depend strongly on the basis set and the tails of the localized molecular orbitals. Second, computational efficiency demands that we block orbitals together so that matrix multiplication can maximize cache utility. Unfortunately, for orbitals i and i' close together in physical space, it is very common for ($ia|ia$) to meet the selection criteria while ($i'a|i'a$) does not. Thus, calculations become very inefficient. These reasons make it impossible to use exchange integrals as the selection criteria.

The obvious alternative to bumping by exchange integrals is bumping by distance between orbitals. On the one hand, bumping by distance has the advantage that it is able to block orbitals together very efficiently. On the other hand, however, bumping by distance has the clear disadvantage of taking only location into account, and not the spatial extent of orbitals.

For these reasons, we have decided to select pairs of orbitals by a hybrid criterion of distance and spatial extent, we call the *bubble* method. We bump the orbital pair ia according to ϕ_{ia} , defined by

$$\sigma_i = \langle i | (\mathbf{r} - \langle i | \mathbf{r} | i \rangle) | i \rangle^{1/2}, \quad (14)$$

$$\sigma_a = \langle a | (\mathbf{r} - \langle a | \mathbf{r} | a \rangle) | a \rangle^{1/2}, \quad (15)$$

$$\phi_{ia} = |\mathbf{r}_i - \mathbf{r}_a| - \lambda_{ia} (\sigma_i + \sigma_a). \quad (16)$$

Here λ_{ia} is a parameter which tells us how to model the spatial extent of localized orbitals. In theory, λ_{ia} can depend on whether the ia pairing is occupied-occupied, occupied-virtual, and virtual-virtual, and whether there is a strong or moderate coupling.^{1,29}

For the present article, we choose $\lambda_{ia}=1$ always, which means that we consider the extent of any localized orbital to be the standard deviation of the wave function. $\lambda_{ia}=2$ would imply two standard deviations (see Fig. 2). Because one standard deviation captures 68% of a Gaussian distribution and two standard deviations capture 95%, for energetic accuracy, we would expect the optimal λ parameter to be somewhere between 1 and 2. For molecules with some tight orbitals and

some very delocalized electronic orbitals, the choice of λ can be critical and this parameterization will be explored in a future paper. For the moment, however, we note that setting $\lambda > 1$ has both advantages and disadvantages. As for the advantages, certainly increasing λ better takes into account orbital extent, and yields a better correlation energy. Moreover, this additional accuracy comes without substantially increasing the exact number of unknown variables, as one efficiently selects amplitudes tied to delocalized orbitals. Unfortunately, there are two strong disadvantages. First, increasing λ to a large value usually leads to an inefficient algorithm because blocking orbitals becomes more difficult. Blocking orbitals is easiest when we block by distance, i.e., $\lambda=0$, and inefficient blocking leads to many wasted FLOPS. Second, as λ grows larger, if one wants to set $c_0=0$ Å (defined precisely below) one finds that the window necessary for obtaining smooth PES's grows. Effectively, the obvious lesson is that orbital variance is not an absolute assessment of orbital locality—the tail of every orbital decays at its own rate. Thus, for chemically smooth PES's (see Sec. VI), one must choose the c_0 and c_1 parameters not too small, and thus, there is not much point in choosing λ close to 2. For these last two reasons, in this paper, we have chosen the most simple bumping approximation of $\lambda=1$.

The pairing bump-function g_{ia} is defined by

$$g_{ia}(\phi_{ia}) = 1, \quad \phi_{ia} < c_1, \quad (17)$$

$$g_{ia}(\phi_{ia}) = \frac{1}{1 + e^{-2|c_1-c_0|/(c_1-\phi_{ia})+|c_1-c_0|/(c_1-\phi_{ia}-c_0)}},$$

$$\phi_{ia} \in (c_1, c_0), \quad (18)$$

$$g_{io}(\phi_{ia}) = 0, \quad \phi_{ia} > c_0. \quad (19)$$

g_{ia} goes smoothly from 1 to 0 as the ia move apart. Note that for the most smoothness, we find one should include the somewhat out-of-place factor of 2 in Eq. (18), to ensure that

we go more slowly from 1 to 0.5, and then more quickly from 0.5 to 0. The form of the one-dimensional bump function should ideally not be important, but we find that a slow decay from 1 is crucial to avoiding wiggles. For a more systematic analysis of the wiggles induced by bump functions, see Ref. 33. For chemical smoothness, we choose the following parameters for our windows:

$$c_1^{\text{strong}} = 0.58 \text{ Å}, \quad c_0^{\text{strong}} = 1.48 \text{ Å}, \quad (20)$$

$$c_1^{\text{medium}} = 2.12 \text{ Å}, \quad c_0^{\text{medium}} = 2.65 \text{ Å}. \quad (21)$$

IV. THE TWICE-BUMPED LCCSD EQUATIONS

For concreteness, we now write down the smoothly twice-bumped local CCSD equations. These equations are twice bumped because we bump both the amplitudes and the Hamiltonian matrix elements (including integrals, Fock elements, and intermediates). We follow very closely the formalism of Stanton *et al.*³⁴ With one exception, the tilde always represents a quantity bumped by the strong bump function as follows:

$$\tilde{t}_i^a = g_{ia}^s t_i^a, \quad (22)$$

$$\tilde{t}_{ij}^{ab} = g_{ijab}^s t_{ij}^{ab}, \quad (23)$$

$$\langle \widetilde{pq} \| uv \rangle = g_{pquv}^s \langle pq \| uv \rangle, \quad (24)$$

$$\widetilde{W}_{pquv} = g_{pquv}^s W_{pquv}, \quad (25)$$

$$\widetilde{\mathcal{F}}_{pq} = g_{pq}^s \mathcal{F}_{pq}. \quad (26)$$

The exception is the Fock matrix which is always bumped by the moderate bump function as follows:

$$\widetilde{f}_{pq} = g_{pq}^m f_{pq}. \quad (27)$$

Explicitly, the iterative equation for T_1 reads

$$D_i^a t_i^a = f_{ia} + g_{ia}^s \left\{ \sum_e \tilde{t}_i^e \widetilde{f}_{ae} (1 - \delta_{ae}) - \sum_m \tilde{t}_m^a \widetilde{f}_{mi} (1 - \delta_{mi}) + \sum_e \tilde{t}_i^e \widetilde{\mathcal{F}}_{ae} - \sum_m \tilde{t}_m^a \widetilde{\mathcal{F}}_{mi} + \sum_{me} \tilde{t}_{im}^{ae} \widetilde{\mathcal{F}}_{me} - \sum_{nf} \tilde{t}_n^f \langle na \| if \rangle - \frac{1}{2} \sum_{mef} \tilde{t}_{im}^{ef} \langle ma \| ef \rangle - \frac{1}{2} \sum_{men} \tilde{t}_{mn}^{ae} \langle nm \| ei \rangle \right\}. \quad (28)$$

For T_2 ,

$$D_{ij}^{ab} t_{ij}^{ab} = \langle ij \| ab \rangle + g_{ijab}^m \left\{ P_-(ab) \sum_e \tilde{t}_{ij}^{ae} \widetilde{f}_{be} (1 - \delta_{be}) - P_-(ij) \sum_m \tilde{t}_{im}^{ab} \widetilde{f}_{mj} (1 - \delta_{mj}) \right\},$$

$$+ g_{ijab}^s \left\{ P_-(ab) \sum_e \tilde{t}_{ij}^e \left(\widetilde{\mathcal{F}}_{be} - \frac{1}{2} \sum_m \tilde{t}_m^b \widetilde{\mathcal{F}}_{me} \right) - P_-(ij) \sum_m \tilde{t}_{im}^{ab} \left(\widetilde{\mathcal{F}}_{mj} - \frac{1}{2} \sum_m \tilde{t}_j^e \widetilde{\mathcal{F}}_{me} \right) + \frac{1}{2} \sum_{mn} \tilde{t}_{mn}^{ab} \widetilde{W}_{mnij} + \frac{1}{2} \sum_{ef} \tilde{t}_{ij}^{ef} \widetilde{W}_{abef} \right.$$

$$\left. + P_-(ij) P_-(ab) \sum_{me} \left(\tilde{t}_{im}^{ae} \widetilde{W}_{mbej} - \tilde{t}_i^e \tilde{t}_m^a \langle mb \| ej \rangle g_{jeba} \right) + P_-(ij) \sum_e \tilde{t}_i^e \langle ab \| ej \rangle - P_-(ab) \sum_m \tilde{t}_m^a \langle mb \| ij \rangle \right\}. \quad (29)$$

The intermediate 2-tensors above are defined as follows:

$$\mathcal{F}_{ae} = -\frac{1}{2} \sum_m \widetilde{f_{me} t_m^a} + \sum_{mf} \widetilde{t_m^f \langle ma \parallel fe \rangle} - \frac{1}{2} \sum_{mnf} \widetilde{\hat{\tau}_{mn}^{af} \langle mn \parallel ef \rangle}, \quad (30)$$

$$\mathcal{F}_{mi} = \frac{1}{2} \sum_e \widetilde{t_i^e f_{me}} + \sum_{en} \widetilde{t_n^e \langle mn \parallel ie \rangle} + \frac{1}{2} \sum_{nef} \widetilde{\hat{\tau}_{in}^{ef} \langle mn \parallel ef \rangle}, \quad (31)$$

$$\mathcal{F}_{me} = \widetilde{f_{me}} + \sum_{nf} \widetilde{t_n^f \langle mn \parallel ef \rangle}, \quad (32)$$

while the intermediate 4-tensors are defined as

$$\begin{aligned} W_{mij} &= \langle mn \parallel ij \rangle + P_{-}(ij) \sum_e \widetilde{t_j^e \langle mn \parallel ie \rangle} \\ &+ \frac{1}{4} \sum_{ef} \widetilde{\hat{\tau}_{ij}^{ef} \langle mn \parallel ef \rangle}, \end{aligned} \quad (33)$$

$$\begin{aligned} W_{abef} &= \langle ab \parallel ef \rangle + P_{-}(ab) \sum_m \widetilde{t_m^b \langle am \parallel ef \rangle} \\ &+ \frac{1}{4} \sum_{mn} \widetilde{\hat{\tau}_{mn}^{ab} \langle mn \parallel ef \rangle}, \end{aligned} \quad (34)$$

$$\begin{aligned} W_{mbej} &= \langle mb \parallel ej \rangle + \sum_f \widetilde{t_j^f \langle mb \parallel ef \rangle} - \sum_n \widetilde{t_n^b \langle mn \parallel ej \rangle} \\ &- \sum_{nf} \widetilde{\hat{\tau}_{jn}^{fb} \langle mn \parallel ef \rangle}, \end{aligned} \quad (35)$$

$$\hat{\tau}_{ij}^{ab} = \widetilde{t_{ij}^{ab}} + \frac{1}{2} g_{ijab}^s (t_i^a t_j^b - t_i^b t_j^a), \quad (36)$$

$$\hat{\tau}_{ij}^{ab} = \widetilde{t_{ij}^{ab}} + g_{ijab}^s (t_i^a t_j^b - t_i^b t_j^a), \quad (37)$$

$$\hat{\tau}_{ij}^{ab} = \frac{1}{2} \widetilde{t_{ij}^{ab}} + g_{ijab}^s t_i^a t_j^b. \quad (38)$$

Here, we have used the standard permutation operators

$$P_{\pm}(pq) = 1 \pm \mathcal{P}(pq), \quad (39)$$

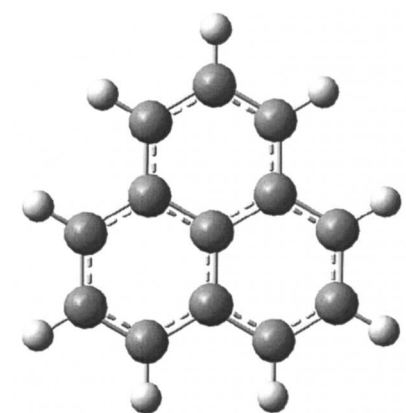
where $\mathcal{P}(p, q)$ permutes the indices p and q . Lastly, we have used D to denote the diagonal Fock matrix energy differences

$$D_i^a = f_{ii} - f_{aa}, \quad (40)$$

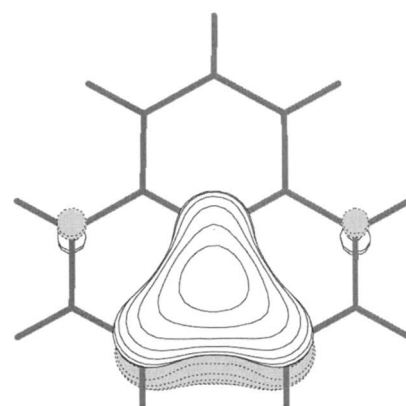
$$D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb}. \quad (41)$$

V. CHEMICAL EXAMPLE: TRICYCLIC PHENALENYL

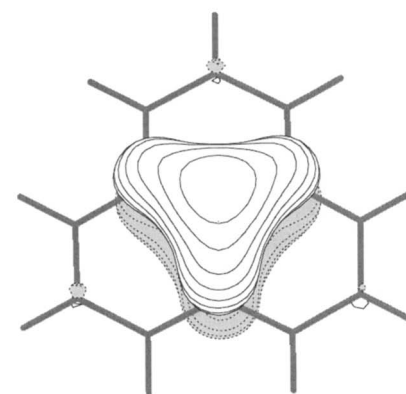
The algorithm described above has been implemented in the Q-CHEM quantum chemistry package.³⁵ We have tested the accuracy of our LCCSD method by measuring the difference in energy between electron attachment and detachment in tricyclic phenalenyl. Tricyclic phenalenyl (shown in Fig. 3) is a medium-sized radical molecule, which has attracted attention as chemists seek to understand and characterize its



(a)



(b)



(c)

FIG. 3. (a) The nuclear geometry of tricyclic phenalenyl. (b) The most delocalized localized orbital of the tricyclic phenalenyl cation (according to the Boys criterion). There are three equivalent localized orbitals of this type for the cation, reflecting the symmetric nature of the molecule. (c) The unique, maximally delocalized localized orbital of the tricyclic phenalenyl anion (according to the Boys criterion). There are no other localized orbitals equivalent to this one, as must be the case given the central location of the localized orbital. The localized orbitals for the anion are very different from those of the cation.

magnetic properties. In 2005, Small *et al.*³⁶ showed that dimers of tricyclic phenalenyl behave erratically and unphysically when analyzed through the lens of density functional theory (with the BLYP functional). In order to capture the electronic structure of the dimer and radical dimer cation even qualitatively, one is forced to use wave function based methods. Perhaps unsurprisingly, the behavior of the localized orbitals of the cation and anion are difficult to under-

TABLE I. A summary of the six different LCCSD algorithms whose results are reported in Tables IIa and IIb. Version 1 is our algorithm from 2006.²⁹ A comparison between versions 1 and 2 reveals the immediate effects of bumping the integrals and intermediates. Version 4 is the chemically smooth, complete LCCSD method we recommend, using the bubble method and the parameterizations from Sec. III. Comparing versions 4, 5, and 6 reveals the additional cost of requiring smooth potential energy surfaces. Version 5 shows the differences between the bubble criterion in comparison to bumping by distance when we ignore smooth PES's, and should be compared with versions 3a and 3b.

LCCSD method	Smoothness	Bumping criterion	Bumping variable (ϕ_{pq})	Strong cutoffs	Bump amplitudes	Bump integrals
Version 1	Mathem. smooth	Distance	\mathbf{r}_{pq}	$c_1=2.90 \text{ \AA}$ $c_0=3.13 \text{ \AA}$	Yes	No
Version 2	Mathem. smooth	Distance	\mathbf{r}_{pq}	$c_1=2.90 \text{ \AA}$ $c_0=3.13 \text{ \AA}$	Yes	Yes
Version 3a	Not smooth	Distance	\mathbf{r}_{pq}	$c_1=c_2=2.64 \text{ \AA}$	Yes	Yes
Version 3b	Not smooth	Distance	\mathbf{r}_{pq}	$c_1=c_2=2.48 \text{ \AA}$	Yes	Yes
Version 4	Chemically smooth	Bubble	$\mathbf{r}_{pq}-(\sigma_p+\sigma_q)$	$c_1=0.58 \text{ \AA}$ $c_0=1.48 \text{ \AA}$	Yes	Yes
Version 5	Not smooth	Bubble	$\mathbf{r}_{pq}-(\sigma_p+\sigma_q)$	$c_1=c_2=0.58 \text{ \AA}$	Yes	Yes
Version 6	Not smooth	Bubble	$\mathbf{r}_{pq}-(\sigma_p+\sigma_q)$	$c_1=c_2=1.48 \text{ \AA}$	Yes	Yes

stand physically. There are no unique Lewis dot diagrams for either the cation or the anion. Rather there are multiple resonant structures, which is often a sign of delocalization.³⁷ Moreover, the localized orbitals of the cation look entirely different from those of the anion. Figures 3(b) and 3(c) show the localized occupied orbitals which are most delocalized in both the cation and anion cases (according to the Boys localization criteria). While the localized π orbitals look somewhat similar, they are quite different and come with totally different symmetry. The cation has three maximally delocalized π orbitals at angles of 120° with each other, while the anion has one maximally delocalized π orbital in the center. Thus, when we compare the energy of the cation versus the anion, we are comparing energies using very different local approximations and strongly testing the validity of our local CCSD model.

We find, however, that according to the parameterization proposed in the previous section, we recover an energy difference which is less than 2 kcal/mol different from the exact CCSD answer, demonstrating the surprising utility of a local correlation algorithm even when not all orbitals are well localized, as is the case for a highly conjugated organic molecule. As a side note, the geometries of the cation and anion have been optimized by RI-MP2 in a cc-pVDZ basis.

A. Energetics

In Table IIa, we report the energies of the cation and anion as computed by LCCSD using different criteria for enforcing locality. Version 1–6 are defined in Table I. Version 1 is our algorithm of 2006,²⁹ which selects and bumps amplitudes entirely by distance. All necessary integrals are computed. Version 2 is the same as version 1, only now we bump the integrals and intermediates, as well as the amplitudes.

As noted earlier, the first crucial result of our calculations to date is that bumping the integrals and intermediates in the LCCSD amplitude equations yields a stable algorithm. So long as one bumps the integrals and intermediates by the same bump function as that used for the strong amplitudes, the algorithm is well conditioned and does not blow up.

Now, unfortunately, bumping the integrals does force the LCCSD algorithm to lose its pseudovariational character. If one bumps only the amplitudes, one almost always finds that the local LCCSD correlation energy is bounded by the exact CCSD correlation energy. Nevertheless, even when bumping integrals, as the constraint of locality is relaxed, the LCCSD energies move almost always monotonically towards the exact CCSD energies. This is a highly desirable feature of any fast, local correlation method.

The second crucial result from our data is that, for all of the test cases studied so far, by bumping integrals in addition to bumping amplitudes, LCCSD correlation energies actually get better, i.e., they move closer to the exact CCSD energy. In other words, the correlation energy from version 2 has consistently been more accurate than the correlation energy of version 1 for all molecules tested so far. This statement has been already been tested on several molecules in their equilibrium geometries as well as transition states. Bumping the integrals apparently rebalances the equations after one has already bumped the amplitudes. Thus, the data suggest that there is no reason why a local correlation algorithm should not bump both the integrals and the amplitudes, though such a statement must still be tested over an expansive and comprehensive range of molecules.

Version 4 is our suggested choice of algorithm, using the bubble selection criteria for locality but using weak cutoffs in order to achieve chemically smooth potential energy surfaces. One should not compare the efficiencies of versions 2 and 4, because version 2 is not chemically smooth—it is only mathematically smooth. This fact was discovered after testing first and second derivatives of potential energy surfaces.

In order to fairly assess the effect of selecting by radius or by the bubble method, one should compare versions 3a, 3b, and 5. These are fast methods which disregard smoothness and aim purely for speed. Versions 3a and 5 run approximately at the same speed and achieve the same amount of accuracy, even though version 3a keeps far more amplitudes (i.e., double) than does version 5 (for the cation). Thus, one finds that the bubble criterion is far better at choosing the

TABLE II. (a) The LCCSD correlation energies for tricyclic phenalenyl as computed by versions 1–6. Versions 1–6 of our LCCSD model are discussed in the text and in Table I. Version 2 is more accurate than version 1, while much faster computationally, suggesting that one should always bump integrals and intermediates, as well as amplitudes. Version 4 is our recommended algorithm and it performs the most accurately of all (though with higher cost too). Future results will show that version 4 also performs best at computing energy barriers. Version 5 is only 1.7 kcal away from version 4, only using much stronger cutoffs, showing the cost of smoothness. Versions 3a and 5 achieve the same accuracy for the same speed, although for different reasons, and version 5 is more stable (as judged by comparing with version 3b). The basis set is cc-pVDZ. The HF energy is $-497.370\,53$ hartree for the cation and $-497.569\,99$ hartree for the anion. (b) The gain in speed when we bump the integrals (as well as the amplitudes) applied to the cationic tricyclic phenalenyl molecule. The exact number is the number of variables that enter the calculation, determining the accuracy of the algorithm. The effective number is the number of variables stored in blocks on disk and in memory, determining the speed of the algorithm. We see that, starting from version 1, one can achieve a speedup of 4 using version 4 or a speed up of 6 using version 2. If one ignores all smoothness, one can gain a speedup of 10 using version 5. Moreover, the computational benefit of bumping integrals will be *much* larger for three-dimensional systems. All calculations were run on a single 2.2 GHz Apple XServe G5 processor with 2 Gbyte random access memory.

(a)	Method	Cation total energy (hartree)	Anion total energy (hartree)	Difference total energy (kcal/mol)	Difference correlation energy (kcal/mol)	Error (kcal/mol)	
	Full CCSD	-499.107 33	-499.361 41	159.4	34.2	0	
	Version 1	-499.098 34	-499.349 51	157.6	32.4	1.8	
	Version 2	-499.110 44	-499.361 52	157.5	32.3	1.9	
	Version 3a	-499.110 47	-499.359 70	156.4	31.2	3.0	
	Version 3b	-499.110 39	-499.351 52	151.3	26.1	8.1	
	Version 4	-499.110 47	-499.361 64	157.6	32.4	1.8	
	Version 5	-499.112 69	-499.361 60	156.2	31.0	3.2	
	Version 6	-499.110 43	-499.362 04	157.8	32.6	1.6	
(b)	Method	Percentage amplitudes exactly (%)	Percentage amplitudes effectively (%)	Percentage integrals exactly (%)	Percentage integrals effectively (%)	CPU time per iteration (s)	Wall time per iteration (s)
	Full CCSD ^a	100	100	100	100	5011	10 193
	Version 1	6.5	18.5	63.1	84.9	4312	11 203
	Version 2	6.5	18.5	5.2	11.0	852	1 819
	Version 3a	3.0	11.6	2.1	7.6	450	1 060
	Version 3b	1.6	11.1	1.1	7.1	382	872
	Version 4	7.7	23.5	9.9	17.9	1392	3 131
	Version 5	1.5	9.4	3.2	7.9	437	1 067
	Version 6	7.7	23.5	9.9	17.9	1392	3 132

^aNote that the full CCSD algorithm was run *with symmetry*, unlike the LCCSD algorithms. Without symmetry, the calculation was far too tedious to wait for exact timings.

important amplitudes than the radial criterion. Moreover, if one looks at the correlation energy as a function of the cutoffs, one finds that, for strong cutoffs, the bubble criterion is far more stable and, in particular, selection by distance can easily fail for the anion, as we see for version 3b. Of course, one should not be very surprised by the poor showing of the radial criterion for the anion, because anions certainly have more diffuse, and less tightly bound, localized orbitals. The strength of the bubble criterion is that it can effectively and efficiently describe the important correlations in the case of an anion. Finally, version 6 is included in order to demonstrate the amount of energetic accuracy that is lost when one bumps away amplitudes for smoothness, which is not very much.

B. Timings

Because our algorithm of 2006 was already near-linear scaling, one may confidently assume that our current implementation scales at least nearly linearly. The more interesting question, however, is how does our new proposed algorithm (version 4) compare in computational cost to its predecessor (version 1). All relevant computational timings are listed in Table II.

The algorithm of 2006 (version 1) was found to have a computational cost with a large prefactor, largely dependent on the number of integrals included in the calculation. Because we have now reduced the number of relevant integrals, we expect that our algorithm will run much faster—which is indeed the case. Indeed, in Table II, if we compare versions 1 and 2, we see that by bumping the integrals and intermediates, all calculations become six times faster. These curves are mathematically, but not chemically smooth. Version 4 is our suggested choice of algorithm, using the bubble selection criteria for locality but using weak cutoffs in order to achieve chemically smooth potential energy surfaces. The bubble selection criterion is far more capable of handling electronic delocalization than bumping by distance (for systems with very large electronic orbitals), and runs four times faster than version 1.

As discussed above, if one seeks to compare timings when selecting by a radial or bubble criterion, one should compare versions 3a, 3b, and 5, where smoothness has been ignored and the algorithms have been found to run at roughly the same speed. Again, for the same amount of computational wall time, version 5 (using the bubble criterion) achieves the same accuracy as version 3a (using the radial

criterion), even though it solves for a few variables. This is primarily because version 3a keeps fewer integrals than version 5, which is a good approximation apparently in these specific calculations. Nevertheless, a robust algorithm that can handle charge delocalization must not rely only on selection of amplitudes by radial distance alone, or one fears one may see the precipitous drop-off as in version 3b.

Finally, in this paper, we have not reported any calculations where we explore bubble selection criteria using $\lambda \neq 1$, see Sec. III. One problem with such criteria is that, although they require a truly minimal exact number of amplitudes for a high degree of accuracy, blocking orbitals becomes difficult and the effective number of amplitudes grows unnecessary large when strong orbital pairs are chosen on the basis of spatial extent and not distance. This is another inconvenient demonstration of the empirical fact that the fastest computational algorithm is not necessarily that one which minimizes the number of necessary FLOPS. For our calculations, we have found that it is important not to rely entirely on a large λ , but to have a medium-sized λ and a reasonably small cutoff c_0 in order to maximize efficiency.

VI. CHEMICALLY SMOOTH POTENTIAL ENERGY SURFACES

The final and most crucial quality of our LCCSD algorithm which must be demonstrated is chemical smoothness of the potential energy surfaces (PES's). While from a mathematical perspective, smoothness is an entirely local property and surfaces may be smooth on the length scale only of femtometers (or smaller), by our own definition above in Sec. I C, chemical smoothness requires no artificial maxima, minima, or inflection points. And although the implicit function theorem guarantees that the potential energy surfaces of our LCCSD algorithm are *mathematically* smooth,²⁸ there is no guarantee of chemical smoothness, which must be checked empirically.

Following the lead of Russ and Crawford,²⁷ we have recomputed potential energy surfaces corresponding to the heterolytic or homolytic dissociation of two molecules. For the heterolytic case, we choose ketene dissociating into singlet methylene and singlet carbon monoxide. For the homolytic case, we choose the unrestricted dissociation of ethane into two CH_3 radicals. These were the examples investigated in 2006,²⁹ when we bumped only the amplitudes and strictly by distance (i.e., $\lambda=0$). In that case, we found apparent smoothness by bumping amplitudes between a window of 2.90 and 3.13 Å (for the strong amplitudes) and 4.10 and 4.43 Å (for the medium amplitudes). A reexamination of those same parameters, however, now shows that those PES's are not chemically smooth according to our new definition (where we must compute first and second derivatives). Nevertheless, we will now show that with the parameterization suggested in Sec. III, we do, in fact, find chemically

smooth potential energy surfaces when we bump both the amplitudes and integrals according to the balloon criterion. All results are shown in Figs. 4 and 5. (Fig. 4 is included in this article and Fig. 5 can be retrieved as an EPAPS document³⁸).

In Figs. 4(a) and 5(a), we show the interesting regions of the dissociation curves for ethane and ketene where cutoffs are crossed and discontinuities are most likely. These are 2.35–3.5 Å for ethane (C–C distance) and 2.04–2.6 Å for ketene (C–O distance). Here, we show the PES's for various different windows. We fix $c_0=0.58$ Å and we allow c_1 to vary. All of the curves shown are formally, mathematically smooth, and they all appear smooth to the naked eye. Nevertheless, when we compute the gradients in Figs. 4(b) and 5(b), we see that an artificial inflection point (or maxima in the gradient) appears when we squeeze $c_1=1.48$ Å into $c_1=1.32$ Å. It is very encouraging that this artificial inflection point appears between the same parameter regimes both for ketene and ethane dissociation. This suggests that one may indeed find a set of parameters which yield both an efficient LCCSD algorithm and produce chemically smooth PES's over a broad range of molecules and nuclear geometries. This last point remains to be numerically tested, but we note that our LCCSD algorithm does give chemically smooth PES's in the case of rotating propane about a C–C bond, showing that chemical smoothness can be achieved both where energetic changes are soft (i.e., rotations) and severe (i.e., bond making and bond breaking).

In order to complete our rigorous analysis of the PES's, we graph in Figs. 4(c) and 5(c) the second derivative of the our LCCSD curves for ketene and ethane. Now, one sees clear oscillations and artificial maxima in our local curves. Clearly, our LCCSD PES's have many points x for which $f''(x)=0$. Such points are inevitable as we approximate the exact CCSD curve—after all, the Taylor approximations of the CCSD and LCCSD PES's must be different at some order. We are satisfied that this difference is large only at third order.

For reference, we show in Figs. 4(d), 4(e), 5(d), and 5(e) the PES's of versions 1, 2, and 6 from Table I. Version 1 is our LCCSD algorithm from 2006, which may now be seen to give mathematically, but not chemically, smooth PES's. Version 2 is the same as version 1, only now bumping integrals as well as amplitudes. As must be expected, version 2 is not chemically smooth. Version 6 is the discontinuous curve, which runs at the same speed as our recommended version 4, but usually attains greater accuracy because it does not bump. Nevertheless, these figures make clear how many and how large are the discontinuities that plague version 6. In particular, version 6 for ketene suffers a discontinuous artificial minimum near 2.53 Å.

Before finishing this section, two final observations should be made about the effect of bumping integrals as well as amplitudes in the LCCSD equations. First, by comparing versions 1 and 2 in Figs. 4(d), 4(e), 5(d), and 5(e), we note that bumping the integrals pushes the version 2 energy closer to the exact CCSD energy than version 1 everywhere along the dissociation curve. Thus, the notion that bumping the integrals partially corrects for the effect of bumping only the

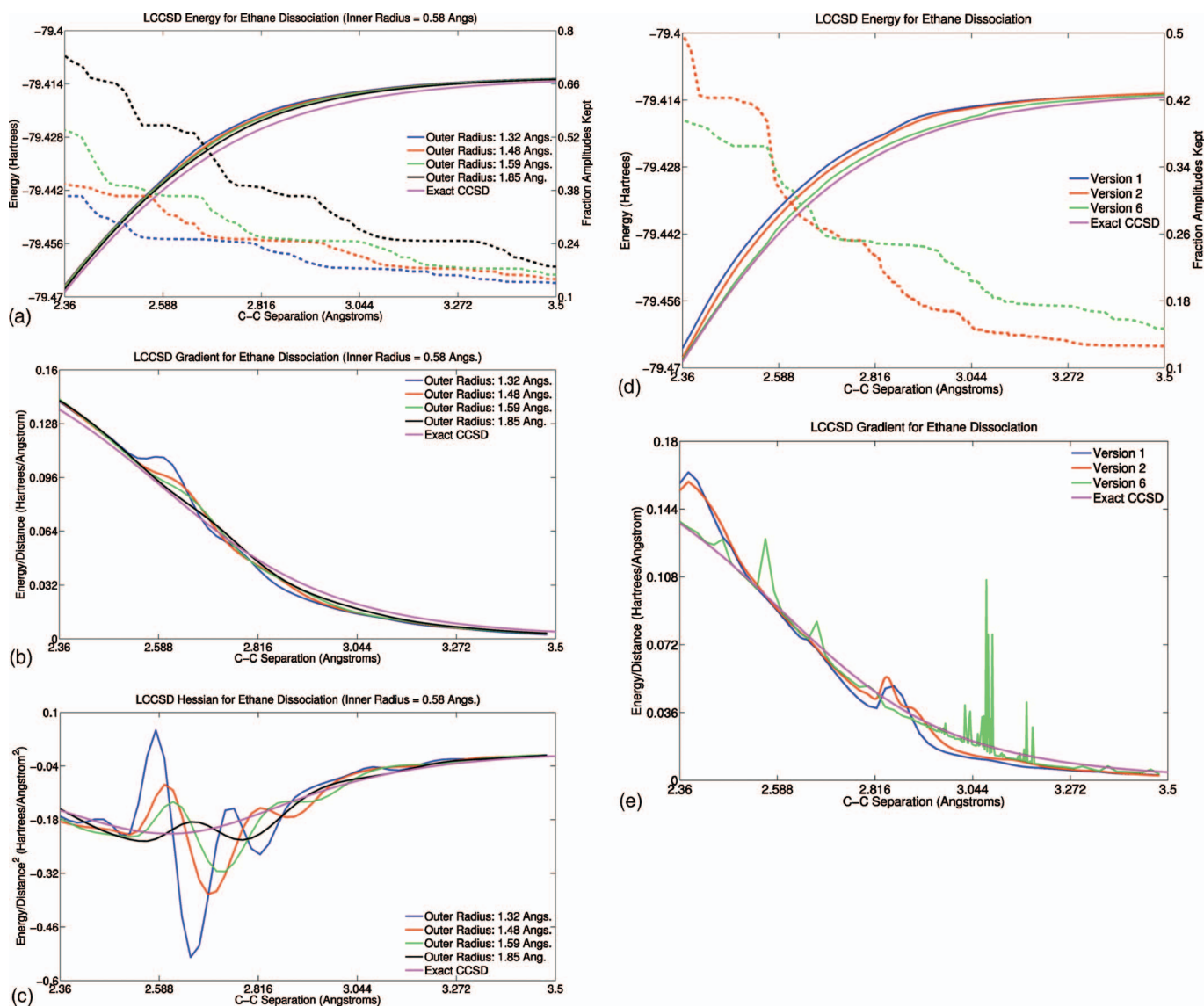


FIG. 4. (Color) (a) The potential energy surface for homolytic, unrestricted ethane dissociation. The basis is cc-pVDZ. Shown are the full CCSD dissociation curves and the LCCSD curves computed for a fixed inner radius c_0 and a variable outer radius c_1 , using the bubble selection criterion. All of the curves “look smooth” at this resolution, and we are forced to look at the gradient if we want to demonstrate chemical smoothness. The dissociation graphs for ketene (Fig. 5) can be accessed via EPAPS (Ref. 38). (b) The gradient of the potential energy surface for homolytic, unrestricted ethane dissociation. One observes that an artificial maximum in the gradient appears for $c_1=1.32$ Å, though one can produce a chemically smooth PES using $c_1=1.48$ Å for this system. (c) The second derivative of the potential energy surface for homolytic, unrestricted ethane dissociation. At this level, one sees large wiggles in the deviations of the local PES from the exact PES. Nevertheless, these wiggles are not too large for $c_1=1.48$ Å, and they never cross zero. (d) The potential energy surface for homolytic, unrestricted ethane dissociation using methods that do not yield chemically smooth PES’s. Versions refer to Table I. Note that versions 1 and 2 are nearly parallel, showing that bumping the integrals does not produce major distortions once the amplitudes have already been bumped. Note also that versions 1 and 2 keep the same number of amplitudes, so the dashed lines for them are the same. (e) The gradient of the potential energy surface for homolytic, unrestricted ethane dissociation using methods that do not yield chemically smooth PES’s. Note that version 1 (our algorithm from 2006) is not chemically smooth, as it has several wiggles in the first derivative. Note, moreover, how many discontinuities exist for version 6. Here, the gradient is computed over a grid with spacing 0.02 Å, except for version 6 between 2.9 Å and 3.2 Å, where we compute the grid with a spacing of 0.002 Å for the sake of more resolution.

amplitudes appears valid not just at equilibrium geometries, but also over a much broader volume of nuclear configuration space. Second, for both heterolytic and homolytic dissociations, bumping the integrals does not distort the PES much more than bumping the amplitudes. This fact is certainly surprising because, whereas bumping the amplitudes decides which orbital groupings $ijab$ to correlate together in a t -amplitude t_{ij}^{ab} , bumping the integrals selects by locality which t_{kl}^{cd} are coupled to which t_{ij}^{ab} . The fact that this second approximation does not lead to larger distortions of the PES is unexpected, and we have no adequate explanation at the current time.

VII. DISCUSSION

This paper has addressed two different, but inter-related questions. First, can we bump the integrals in the LCCSD equations and make a faster algorithm without losing much accuracy and achieving chemically smooth PES’s? Second, what is the best criteria for selecting the amplitudes, integrals, and other Hamiltonian matrix elements? We now address these questions in turn.

First, regarding the bumping of integrals, for many years, the largest criticism of the Saebø-Pulay-Schütz-Werner LCCSD algorithm was that the LCCSD potential en-

ergy surfaces were discontinuous.²⁷ Although Mata and Werner have presented a solution for smooth PES's whereby one merges domains,³⁹ their approach requires chemical intuition of the program user, can yield hysteresis, and is not ultimately satisfying. Now, mathematically, the smoothness problem can be solved²⁸ by bumping the amplitude equations—again, the implicit function theorem makes very few demands if all we seek is mathematical smoothness of the potential energy surface. However, there remains the problem of what is the correct way to bump the equations, so that one maintains accurate PES's, while inheriting the fewest unphysical distortions and finding chemically smooth potential energy surfaces. Maintaining a highly accurate potential energy surface, with accurate first and second derivatives, is clearly much more difficult than achieving only a fast local approximation. One clear conclusion from this paper, though, is that with the right choice of bump functions and bumping parameters, chemically smooth PES's can be achieved while the amplitudes and integrals are simultaneously bumped.

Regarding the smoothness and stability of our local algorithm, one crucial observation we have made is that the stability of any local algorithm will be compromised if one considers all of the different bumping parameters to be independent variables. Stability requires that one bump the integrals less stringently than the amplitudes. Furthermore, if one is to bump the integrals, then one should also bump the intermediates with the same stringency. If one allows the different bump functions to be independently varied, one can get correlations which are both far too high and far too low. Our local CCSD algorithm works well because of the natural cancellation of errors that arises when we use only one strong and one moderate bump function to bump a number of different variables. Once we insist on the uniformity of the bump function, our LCCSD algorithm is quite stable and, in all examples so far, the data only get better as one relaxes the cutoffs.

Regarding the accuracy of our method, the most astonishing conclusion of this paper is the high level of energetic accuracy rendered by our LCCSD algorithm even after bumping the integrals. We could not have predicted *a priori* that when ab and ef are not close to each other, one can ignore the coupling between t_{ij}^{ab} and t_{ij}^{ef} , which are formally coupled in the CCSD equations through $\langle ab||ef \rangle$. The success of our twice-bumped LCCSD algorithm emphasizes how broadly one may invoke locality when computing the electronic correlation in many molecular systems, and suggests that future local correlation algorithms may introduce yet more approximations of locality in order to reduce computational cost.

Second, regarding the selection criteria, our experience with the tricyclic phenalenyl anion and cation demonstrates the importance of selecting orbital pairs based both on centroid position and orbital extent. In this paper, we have shown that, for a given fixed number of amplitudes, one can achieve more accuracy if one accounts for the spatial extent of localized orbitals. Although, for many insulators, one can achieve the same accuracy with the same computational wall time whether one selects for amplitudes based on the radial

criterion or the bubble criterion, we note that the radial criterion can be pushed out of range more easily than the bubble criterion, as seen comparing versions 3a and 3b.

Moreover, we have gathered enough a lot of unpublished evidence showing that an algorithm based purely on radial selection can fail when the localized orbitals become even bigger than they are in tricyclic phenalenyl. In that case, the largest localized orbitals for tricyclic phenalenyl have standard deviation 1.5 Å and the smallest, noncore orbitals are of size 0.75 Å. This twofold difference is not that large, especially if we bump with a distance cutoff of 3.13 Å. If we seek a stable LCCSD algorithm which is applicable to interesting molecules, especially those with weakly bound electrons or electrons being transferred, and over the entire PES, we have no choice but to bump orbitals not just by distance but also by spatial extent for accuracy. In particular, if we choose a geometry wherein some localized orbitals have standard deviation larger than 3 Å, bumping by distance only would obviously be a terrible approximation.

Finally, we now mention that the two central issues of this paper are very connected. In particular, one reason to use the bubble method for pair selection is because orbitals vary in spatial extent, and some electronic orbitals cannot be well localized. For such cases, bumping by distance only would not be accurate at all. However, if we use the bubble method, we are actually *forced* to bump the integrals if we want to achieve a linear-scaling LCCSD algorithm. This can be seen as follows: Suppose we consider a charge-transfer transition state or a loosely bound radical anion, labeling i as the most delocalized electronic orbital. Suppose further that i is so weakly bound, that i overlaps with all of the virtual orbitals c , and the bubble method correctly selects all ic for strong amplitude coupling. In that case, if we were not to bump the integrals, Fig. 1(a) shows us that we must compute all N^4 of the virtual integrals, since all virtual orbitals a and b are connected by orbital i . Thus, in order to achieve linear scaling, one is forced to bump the integrals.

This necessarily raises the very interesting theoretical question as to whether or not a local correlation algorithm can be applied successfully to systems with electronic delocalization. Let a and b be two localized virtual orbitals, far apart from each other. Because i is delocalized, according to the bubble method, we explicitly solve for both the t_{ii}^{aa} and t_{ii}^{bb} amplitudes. However, when we bump the integrals, these amplitudes are not directly coupled in the LCCSD equations, because the integral $\langle a\bar{a}||b\bar{b} \rangle$ is bumped to zero. Our local CCSD algorithm couples these two excitations only indirectly through other excitations. The evidence presented in this paper suggests that bumping the integrals usually makes the local approximation even better for tricyclic phenalenyl, an organic molecule with lots of conjugation. However, can such a statement hold true for an anion or a transition state with much greater charge delocalization? Our unpublished data for a charge-transfer transition state suggest that the answer is yes. We are gathering additional data demonstrating that locality in the ground state may be even more ubiquitous than we had previously thought. In such a case, local correlation theory may find itself useful in a much broader

arena of quantum chemistry, perhaps even electronic transport, where there are mixtures of localized and delocalized electronic degrees of freedom.

VIII. CONCLUSIONS

This paper demonstrates that, in developing a LCCSD algorithm, one may bump the integrals (and other Hamiltonian matrix elements) in addition to bumping the amplitudes (which was the original proposal for an LCCSD algorithm²⁸). Bumping the integrals reduces the computational cost of one calculation while actually *increasing* the accuracy of the algorithm. For interesting molecules, we have argued that one must select the most important amplitudes and integrals both by the location and the spatial extent of localized orbitals, in order to minimize computational cost. Finally, our smoothed LCCSD algorithm does not introduce artificial stationary points or inflection points into the potential energy surfaces, achieving what we call chemically smooth surfaces.

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