

and oversaturated regimes. Moreover, locally disordered regions in Potts models act as effective vacancies, and by condensing cause first-order phase transitions.¹⁴ Effective vacancies are favored by competing helicity (in the fluid dip region of the phase diagram) and could conceivably produce tricritical and triple points [insets Figs. 3(a) and 5]. Finally, by treating triangular patches forming a hexagonal array, the possibility of striped^{5a} domain-wall phases would also be included.

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Novel *Ab Initio* Correlated Calculations for an Infinite Chain of Hydrogen Atoms

R. D. Poshusta

Chemical Physics Program, Washington State University, Pullman, Washington 99164

and

D. J. Klein

Department of Marine Sciences, Texas A & M University at Galveston, Galveston, Texas 77553

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A novel cluster-expanded *ab initio* effective or model Hamiltonian is described and illustrated for a linear chain of hydrogen atoms. The method relies on expanding the model Hamiltonian in a sum of irreducible cluster interaction operators. A hierarchy of increasingly accurate *ab initio* Heisenberg spin Hamiltonians duplicate low eigenvalues of the more complete Schrödinger Hamiltonian. Finally these Heisenberg models are treated to obtain the ground-state energy and magnetic susceptibility of the infinite chain.

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Most conventional theories of extended systems rely on a delocalized independent-particle viewpoint. We here show a method which adopts the localized viewpoint (successful in even pre-quantum-mechanical solid-state theories) and combines an expansion in terms of clusters (the localized entities) with *ab initio* correlated calculations on the clusters. This straightforward approach was indicated in low-order approximation

for the Hubbard model by Bulaevski.¹ A more detailed description of our method, including its relation to other more conventional approaches, is to be reported elsewhere.² Here we illustrate the essential features of our method for one-dimensional chains of hydrogen atoms.

The method combines *ab initio* results for small subunits of an infinite system with a cluster expansion. The *ab initio* calculations may be per-

formed by any reliable method. For small systems a large configuration-interaction (CI) wave function can yield most of the correlation energy in each cluster. It is, of course, important that results be of comparable accuracy for every cluster. We calculate a model Heisenberg spin Hamiltonian for each cluster by requiring the model cluster to have the same energy spectrum as the *ab initio* calculation. The model Hamiltonian is expanded in a complete set of irreducible cluster-interaction operators. Convergence is recognized by the decreasing contributions made as clusters grow larger. Truncation to dominant cluster-interaction operators gives an approximate *ab initio* model Hamiltonian which in turn is to be solved.

For the linear chain of hydrogen atoms each cluster is a subchain. We let the graph-theoretic symbol Γ represent a sequence of N sites connected by nearest-neighbor bonds (or graph-theoretic edges). Subchains or clusters $\gamma \in \Gamma$ are labeled by the subsequences of sites in γ . Chains and subchains of equally spaced sites such as here are completely specified by their sizes which we write as $|\Gamma|=N$ and $|\gamma|$.

Accurate energy values and wave functions are readily found for small clusters, such as, in our present example, linear H atom chains through $N=6$. Our method will be illustrated by use of two variational wave functions: The first, (a), is a CI wave function of all covalent and ionic structures composed from unoptimized hydrogenic $1s$ orbitals on each site; the second, (b), is the same type of CI space now using (orbital exponent) optimized $1s$ orbitals. Greater accuracy could be achieved by extending the orbital basis. A key point in our choice of CI spaces is that the spaces be chosen such that they can be viewed as being spanned by all (particle conserving) products formed from a set of site states. Here there are four possible site states on each site, namely, H^+ , $1s\alpha$, $1s\beta$, and $1s^2$.

We will utilize the energies of several low-lying states of each spin multiplicity. For example, we need the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2 , and two doublet states and one quartet of H_3 . Our results for these subchains or clusters are intermediate between Hartree-Fock (HF) and exact values. For cluster length $N=2$ (H_2 at $R=1.886$ bohrs), the ground-state energy in each approximation is, for Hartree-Fock (HF), -1.101 a.u. (Ref. 3); for (a), -1.112 a.u.; for (b), -1.125 a.u.; exact,³ -1.146 a.u.

We shall make a cluster expansion of a model

Hamiltonian $\mathcal{K}(\Gamma)$ for system Γ . A first general condition on $\mathcal{K}(\Gamma)$ is that it be defined on a space spanned by products of site states, these site states corresponding to subsets of those used in the CI calculations. A second general condition to be imposed is that $\mathcal{K}(\Gamma)$ have eigenvalues agreeing exactly with the corresponding low-lying eigenvalues arising from a CI calculation. In this way we regard $\mathcal{K}(\Gamma)$ as an *ab initio* model representation of low-lying CI eigenlevels of Γ , and approximations to $\mathcal{K}(\Gamma)$ yield approximations to those CI eigenlevels.

For the H-atom chain we choose the site states to be up and down spins on each site; thence $\mathcal{K}(\Gamma)$ can be viewed as a Heisenberg spin Hamiltonian defined on the 2^N -dimensional space of spin orientations ($\pm \frac{1}{2}$) for each of the N atoms. For well-separated atoms this space is certainly reasonable. Regardless of separation this space corresponds to the (covalent) valence-band space such as introduced by Heitler and London. In addition our results can surpass the Heitler-London approximation, since $\mathcal{K}(\Gamma)$ includes the affects of CI with higher-lying states. The matching between the low-lying CI eigenlevels and those of $\mathcal{K}(\Gamma)$ is to be achieved by an appropriate choice for the so-called "exchange parameters" appearing in $\mathcal{K}(\Gamma)$.

We express $\mathcal{K}(\Gamma)$ in terms of permutations,

$$\mathcal{K}(\Gamma) = \sum_P J_P(\Gamma) P, \quad (1)$$

where $J_P(\Gamma)$ is termed an exchange (or permutation) energy. The permutations P may be transcribed into spin operators $\vec{S}_i \cdot \vec{S}_j$ via the Dirac identity,⁴ since the sum in Eq. (1) may be⁵ restricted to transpositions and products of disjoint transpositions. Further, many of the J 's are equal by symmetry [e.g., for $\Gamma=(1,2,3)$ we have $J_{(12)}(\Gamma) = J_{(23)}(\Gamma)$].

Assuming that $\mathcal{K}(\Gamma)$ is given we make the cluster expansion

$$\mathcal{K}(\Gamma) = \sum_{\gamma \in \{\Gamma\}} V(\gamma) \quad (2)$$

in a complete set $\{\Gamma\}$ of connected subgraphs of Γ . Here $V(\gamma)$ is called the *irreducible cluster interaction* belonging to γ . Equations (2) for each possible graph Γ form a linear transformation which may be inverted to give (for linear chains)

$$\begin{aligned} V(i) &= \mathcal{K}(i), \\ V(i, i+1) &= \mathcal{K}(i, i+1) - \mathcal{K}(i) - \mathcal{K}(i+1), \\ V(i-1, i, i+1) &= \mathcal{K}(i-1, i, i+1) - \mathcal{K}(i-1) - \mathcal{K}(i) - \mathcal{K}(i+1) + \mathcal{K}(i), \end{aligned} \quad (3)$$

etc. Inversions for more general graphs may be effected by Möbius functions.⁶ Cluster interactions are also expressed in permutations:

$$V(\gamma) = \sum_P j_P(\gamma) P, \quad (4)$$

where $j_P(\gamma)$ is an irreducible cluster exchange energy.

The (*ab initio*) model Hamiltonian $\mathcal{K}(\Gamma)$ and the irreducible cluster interactions $V(\gamma)$ are determined exactly in a stepwise fashion. In the first step with Γ consisting of a single site our *ab initio* basis determines the H-atom energy $E(1)$. The eigenvalue of $\mathcal{K}(1)$ is $\epsilon(1) = J_1(1) = j_1(1)$ so that the exchange energies are completely fixed by requiring $\epsilon(1) = E(1)$. In the second step (1,2) there are two *ab initio* eigenvalues $E(^1\Sigma_g^+)$, the singlet ground state, and $E(^3\Sigma_u^+)$, the triplet. The eigenvalues of $\mathcal{K}(1,2)$ are $^1\epsilon = J_1(1,2) + J_{(12)}(1,2)$ and $^3\epsilon = J_1(1,2) - J_{(12)}(1,2)$. The requirements $^1\epsilon = E(^1\Sigma_g^+)$ and $^3\epsilon = E(^3\Sigma_u^+)$ give two equations to fix the values of J_1 and $J_{(12)}$. Next Eqs. (3) determine $j_1(1,2)$ and $j_{(12)}(1,2)$, and so forth.

For linear chains through $N=3$ the operators $\mathcal{K}(\Gamma)$ and $V(\gamma)$ and the interaction energies $J_P(\Gamma)$ and $j_P(\gamma)$ are uniquely determined by equality of \mathcal{K} and *ab initio* eigenvalues of corresponding symmetries. Additional constraints are necessary for $N \geq 4$. Here we choose to constrain $V(\gamma)$ to be "small"; that is we minimize the operator norm $\|V(\gamma)\|$ where $\|V\| = \text{tr} V^\dagger V$.

Convergence of the cluster expansion may be empirically assessed in several ways. The contributions to a given exchange energy tend to decrease as the cluster size increases, e.g., $j_{(12)}(1,2) = 0.147$, $j_{(12)}(1,2,3) = 0.021$, and $j_{(12)}(1,2,3,4) = 0.002$ [at the (a) level of approximation]. Also the operator norm of the irreducible cluster interaction decreases with cluster size, e.g., $\|V(1,2)\| = 0.113$, $\|V(1,2,3)\| = 0.016$, $\|V(1,2,3,4)\| = 0.005$ [at the (b) level]. Evidently, at $R = 1.886$ bohrs, the cluster expansion converges slowly.

The irreducible cluster interactions are next used to construct an n -site approximation to $\mathcal{K}(\Gamma)$ for very long cyclic chains. Namely, we truncate the cluster expansion by neglecting clusters above the size $|\gamma| = n$:

$$\mathcal{K}^{(n)}(\Gamma) = \sum_{|\gamma| \leq n} V(\gamma). \quad (5)$$

For $n=2$ we have merely a nearest-neighbor Heisenberg model for which the ground-state energy of an infinite cyclic chain was given by Hulthén.⁷ For $n=3$ we have a next-nearest-neighbor Heisenberg model for which the ground-state energy of

an infinite cyclic chain has been estimated by Garani *et al.*⁸ For $n=4$ we estimate the ground-state energy of an infinite chain in the same way (extrapolating finite-cycle results on a plot of E/N versus $1/N^2$). Our results for both $N=6$ and $N \rightarrow \infty$ cycles are given in Table I. For comparison we give values computed by other methods,⁹⁻¹⁶ mostly either the restricted or unrestricted HF (RHF or UHF) methods.

The spin states of our Heisenberg model correspond to those of the CI wave function. Hence the CI spin magnetic properties are accurately represented by those of $\mathcal{K}(\Gamma)$. Therefore we may use earlier work on the nearest-neighbor¹⁸ and next-nearest-neighbor¹⁸ Heisenberg models to estimate the zero-temperature magnetic susceptibility χ_0 of hydrogen chains. The two- and three-site approximations yield values of

TABLE I. *Ab initio* ground-state binding energies per site for cyclic chains of hydrogen atoms. n -site denotes our cluster expansion truncated to n -site interactions.

Method	Ref.	N	R (a.u.)	a	b
RHF	10	6	2.00	0.53021	0.53456
UHF	10	6	2.00	0.53700	0.54300
CI	9	6	2.00	0.54160	0.54803
CI	17	6	2.00		0.54157
2-site		6	2.00	0.53376	0.54041
3-site		6	2.00	0.54595	0.54983
4-site		6	2.00	0.54209	0.54739
2-site		6	1.886	0.52993	0.539029
3-site		6	1.886	0.54380	0.54965
4-site		6	1.886	0.53795	0.55242
RHF	13	14	1.888		0.53232
RHF	13	38	1.886		0.53011
RHF	13	62	1.886		0.52978
RHF	13	14	1.888		0.53857 ^c
~HF	11	∞	2.00	0.4915	
HF	12	∞	2.00	0.5195	
RHF	15	∞	1.88		0.52385
RHF	15	∞	1.78		0.52660
RHF	16	∞	1.95		0.52939
UHF	16	∞	1.95		0.53139
2-site		∞	1.886	0.52286	0.53168
3-site		∞	1.886	0.53693	0.53331
4-site		∞	1.886	0.53160	0.54485
RHF	14	∞	1.95		0.5341 ^c
UHF	14	∞	1.95		0.5384 ^c

^aCalculations restricted to the CI space constructed from unscaled 1s orbitals.

^bCalculations within the CI space constructed from scaled 1s orbitals.

^cCalculations using a double-zeta basis of orbitals.

$\chi_0/Ng^2\mu_B^2 = 0.344$ and 0.39 a.u. for the (b) space, where g and μ_B are the spin g factor and Bohr magneton. Magnetic susceptibility has not been reported for previous *ab initio* calculations. Of course additional properties can be obtained by use of the Heisenberg model, even above absolute zero.

We have illustrated a localized-site cluster-expansion method for infinite periodic systems by application to chains of H atoms. Correlation is explicitly included, so that our energies lie below the corresponding RHF and UHF results. Extrapolated energies for chains of length $N = 6$ are consistent with full CI *ab initio* results. Our method appears to converge to the exact values as longer clusters are included (four-site approximation better than three-site, etc.).

The Heisenberg Hamiltonians utilized have a familiar magnetic interpretation. In the nearest-neighbor or two-site approximation our model indicates an "antiferromagnetic" interaction $J_{(12)} > 0$ between H atoms which agrees with more accurate results^{9,17} for finite chains.

Our method can be extended and improved in several ways. (1) Any small-system *ab initio* (or empirical or experimental) method can be used to find the requisite energy values. (2) Cluster interactions can be found in two and three dimensions by appropriate modifications in Eq. (4). (3) The "sites" of the method can be any atom or molecule. (4) More than one type of site or "bond" may be present in the lattice. (5) The model Hamiltonian may be changed to, say, a Hubbard model.

The two internal methods to assess accuracy cited here and comparison with previous work provide empirical justification for our truncated cluster-expansion method. We feel that the meth-

od will in practice be rapidly convergent for a wide variety of systems in view of our present calculations on a system of H atoms at a relatively small separation where the atoms are very strongly interacting in comparison with what is ordinarily regarded to be treatable by the Heisenberg model.

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