

# Charge renormalization at the large- $D$ limit for diatomic molecules

R. Bleil, A. Falijs, M. Miletic, and S. Kais

*Department of Chemistry, Purdue University, West Lafayette, Indiana 47907*

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The charge renormalization procedure for the calculation of the correlation energy of atoms utilizing the analytically known large- $D$  limit solutions for the exact and Hartree–Fock equations is extended to diatomic molecules. This procedure is based on the variation of the nuclear charge,  $Z$ , and internuclear distance,  $R$ , of the Hartree–Fock Hamiltonian such that the Hartree–Fock energy will be significantly closer to the exact energy. We calculate to first order in  $\delta Z$  the leading contribution to the correlation energy by changing the nuclear charge to some renormalized nuclear charge,  $Z_i^R \rightarrow Z_i + \delta Z_i$ . To first order in  $\delta Z$ , this leads to an approximate expression,  $E^{\text{corr}}(Z_a, Z_b, R) = (\partial E^{\text{HF}}/\partial Z_a) \delta Z_a + (\partial E^{\text{HF}}/\partial Z_b) \delta Z_b$ , for the correlation energy based on the charge renormalization parameter  $\delta Z$ , which is fixed systematically from the large- $D$  limit. The theory is applied to diatomic molecules. Near the equilibrium, we are predicting the correlation energy typically with 80% or greater accuracy in a completely self-consistent and systematic way with no additional cost to the Hartree–Fock calculation. An improved approach to estimating the correlation energy for all  $R$  is outlined. © 1995 American Institute of Physics.

## I. INTRODUCTION

At present, the major approach for quantitative calculations of many electron systems remains the Hartree–Fock self-consistent field approximation.<sup>1</sup> Hartree–Fock calculations usually give good total energies for most atoms and molecular systems. However, the remaining error relative to the exact total energy, the correlation energy, is very important in atoms, and the effects of the correlation energy are even more dramatic in molecules, because this energy is of the same order as a chemical bond.

For bound molecular systems, the Hartree–Fock method accurately predicts the geometry of the minimum energy structure. For open shell and weakly bound systems, the Hartree–Fock method often fails to give the correct dissociation limit.<sup>2</sup> For van der Waal's systems, such as the rare gas clusters and van der Waal's complexes, the Hartree–Fock method fails to predict a minimum.<sup>3</sup>

Because of these difficulties, much work has been done to improve the accuracy of these self-consistent field calculations by the inclusion of perturbation theory (as in the MP2 and MP4 theories), and higher order theories, such as configuration interaction (CI), coupled cluster theory (CC),<sup>4</sup> and density functional theory (DFT).<sup>5</sup> These methods significantly improve the Hartree–Fock energy, however, they are much more computationally expensive. The formal cost of high level *ab initio* methods scales at least as  $N^5$ , where  $N$  is the number of atomic orbital basis functions, making them impractical for large molecular systems. Because of the extreme cost of the traditional correlated electronic structure methods for large systems, there is a growing effort to introduce new electronic structure methods to meet the objective of accounting for the correlation energy with minimal additional cost relative to Hartree–Fock calculations.

Dimensional scaling offers an effective means to treat many-body problems involving nonseparable interactions of strongly correlated particles.<sup>6</sup> The dimensional renormalization approach utilized in the past has proven to be very suc-

cessful in the treatment of the ground state and electronic properties, such as ionization potential and electron affinities, for  $N$ -electron atoms.<sup>7,8</sup> The previous procedure differs from the approach taken in this publication in that the charge renormalization has been utilized to equate the Hartree–Fock energy in three dimensions to the large- $D$  Hartree–Fock energy. This renormalized charge was then substituted into the large- $D$  limit for the exact energy, from which the three dimensional energy was approximated.<sup>9</sup> In the present approach, we renormalized the charge such that the Hartree–Fock energy equals the exact energy in the large- $D$  limit. We then use this large- $D$  limit charge renormalization to correct the Hartree–Fock energy in three dimensions.

In a recent publication,<sup>10</sup> we have shown a means for predicting the correlation energy for atoms by using the large dimensional limit results. Because the Hartree–Fock method averages over the electron–electron interaction term, we assumed that we could correct for correlation energy by compensating this for change by finding an effective nuclear charge,  $Z^R = Z + \delta Z$ . To avoid making  $\delta Z$  an arbitrarily adjustable parameter, we took advantage of the fact that both the Hartree–Fock and exact Schrödinger equations have been solved analytically in the large- $D$  limit.<sup>11</sup> By utilizing these analytical solutions, we could find a renormalized charge,  $Z + \delta Z_\infty$ , which corrects for the correlation energy in the large- $D$  limit. This procedure recovered more than 80% of the correlation energy for several atoms and ions and corrected the results for the weakly bound system  $\text{H}^-$  sufficiently such that with our procedure, this anion was found to be stable, while standard Hartree–Fock calculations predicts it to be unstable.

In this paper, we expand this theory and apply our approach to diatomic molecules. For application of charge renormalization to molecules, it becomes necessary to account for the variation of the correlation energy as a result of varying the internuclear distance. In the leading order term for our correlation energy formulation for molecules, we need only the partial derivative of the Hartree–Fock energy

with respect to the nuclear charge, which is calculated using the Hellmann–Feynman theorem. In this way, we assume the renormalization parameter  $\delta Z$  will be a constant with respect to internuclear distance  $R$  and can be taken from the large- $D$  limit. This procedure predicts the correlation energy with no additional cost to the Hartree–Fock calculation.

The outline of this paper shall be as follows: in Sec. II, we will discuss the theory behind using effective nuclear charges for molecules; in Sec. III we discuss the details of our Hartree–Fock calculations; we review in Sec. IV how to calculate the effective nuclear charge  $\delta Z_\infty$  for  $N$ -electron atoms; these effective nuclear charges are applied to many diatomic molecules in Sec. V; in Sec. VI we discuss our approach to solving for  $\delta Z(R)$ ; finally, we outline in the discussion in Sec. VII further plans for correcting the dissociation limit based on the work we have done to date.

## II. THEORY

Our goal is to find a systematic way to vary the Hartree–Fock parameters which will have the effect of causing the Hartree–Fock calculation to more accurately predict the exact values. For molecular systems, we can vary the set of the nuclear charges  $\{Z_i\}$  on each atom  $i$  and the internuclear distances  $\{R_{ij}\}$  between each pair of atoms  $i$  and  $j$ . We choose to vary the nuclear charges by the addition of some small correction term resulting in a renormalized nuclear charges  $\{Z_i^R = Z_i + \delta Z_i\}$  and the internuclear distances  $\{R_{ij}^R = R_{ij} + \delta R_{ij}\}$ . Expanding the renormalized Hartree–Fock energy to first order in  $\delta Z$  and  $\delta R$  gives

$$E^{\text{corr}}(\{R_{ij}\}, \{Z_i\}) = \sum_i \frac{\partial E^{\text{HF}}}{\partial Z_i} \delta Z_i + \sum_{i < j} \frac{\partial E^{\text{HF}}}{\partial R_{ij}} \delta R_{ij} \quad (1)$$

as our expression for the correlation energy.

To calculate the derivative of the energy with respect to a parameter, say  $\lambda$ , ( $\partial E / \partial \lambda$ ), we will start with the general matrix equation  $\mathbf{MC} = 0$ , where the self-adjoint matrix  $\mathbf{M}$  is defined by the Hamiltonian matrix  $\mathbf{H}$ , and the overlap matrix  $\mathbf{S}$  by<sup>12</sup>

$$M_{\mu\nu} = H_{\mu\nu} - ES_{\mu\nu}, \quad (2)$$

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial \mathbf{H}}{\partial \lambda} - E \frac{\partial \mathbf{S}}{\partial \lambda} \right\rangle \quad (3)$$

for homonuclear diatomic molecules, which is the subject of this paper, for  $\lambda = R$  we obtain the virial theorem and for  $\lambda = Z$  we get the Hellmann–Feynman theorem.

Because at the asymptotic limit as well as at exact equilibrium distance, ( $\partial E^{\text{HF}} / \partial R$ )  $\approx 0$ , we expect the leading contribution to the correlation energy for diatomic molecules to be

$$E^{\text{corr}}(Z_a, Z_b, R) \approx \frac{\partial E^{\text{HF}}}{\partial Z_a} \delta Z_a + \frac{\partial E^{\text{HF}}}{\partial Z_b} \delta Z_b. \quad (4)$$

The increment in the effective nuclear charge,  $\delta Z$ , is taken to be the large- $D$  limit,  $\delta Z_\infty$ , for each individual atom in the molecule, which has been determined previously for atoms by matching the large- $D$  limit Hartree–Fock solution with  $Z + \delta Z_\infty$  with the exact large- $D$  limit solution.<sup>10</sup>

TABLE I. Comparison of the correlation energy from Eq. (6) with the exact values.

| Atom            | State | $\frac{\partial E^{\text{HF}}}{\partial Z}$ | $\Delta Z_\infty^a$ | $-E_\infty^{\text{corr}}$ | $-E_{\text{exact}}^{\text{corr} \ b}$ | % Error |
|-----------------|-------|---|---------------------|---------------------------|---------------------------------------|---------|
| He              | $1S$  | 3.372 968                                   | 0.008 173           | 0.027 567                 | 0.042 20                              | 34.4    |
| Li              | $2S$  | 5.715 354                                   | 0.007 207           | 0.041 190                 | 0.045 33                              | 9.1     |
| Be <sup>c</sup> | $1S$  | 8.407 457                                   | 0.007 224           | 0.060 735                 | 0.094 34                              | 35.6    |
| B <sup>c</sup>  | $2P$  | 11.383 529                                  | 0.007 552           | 0.085 968                 | 0.124 85                              | 31.1    |
| C <sup>c</sup>  | $3P$  | 14.694 444                                  | 0.007 984           | 0.117 320                 | 0.156 40                              | 24.9    |
| N               | $4S$  | 18.341 14                                   | 0.008 445           | 0.154 890                 | 0.188 31                              | 17.7    |
| O               | $3P$  | 22.265 573                                  | 0.008 900           | 0.198 163                 | 0.257 94                              | 23.1    |
| F               | $2P$  | 26.525 608                                  | 0.009 337           | 0.247 669                 | 0.324 53                              | 23.6    |
| Ne              | $1S$  | 31.120 268                                  | 0.009 750           | 0.303 422                 | 0.390 47                              | 22.2    |

<sup>a</sup>See Ref. 10.

<sup>b</sup>Exact values taken from Ref. 18.

<sup>c</sup>Correcting these values to  $E^{\text{CAS}}$  to account for the configuration mixing reduces the error of Be to 20%, B to 4.5%, and C to 14%. See Ref. 10 for details.

## III. HARTREE–FOCK COMPUTATIONS

To calculate the term ( $\partial E^{\text{HF}} / \partial Z$ ), necessary for the calculation of the correlation energy, we used the Hellmann–Feynman theorem which yields

$$E^{\text{corr}}(R_{ab}, Z_i) \approx - \sum_a \delta Z_a \mathbf{U}^T \mathbf{D}_T + \frac{Z_a \delta Z_b + Z_b \delta Z_a}{R_{ab}}, \quad (5)$$

where the  $\delta Z$  is calculated from the atomic limit and are given in Table I,  $\mathbf{U}^T$  is the Hermitian matrix of the electron–nucleus potential energy term in the Hamiltonian, and  $\mathbf{D}_T$  is the total electron density matrix.<sup>13</sup>

The calculation of the correlation energy was done on a modified program by Gomperts and Clementi based on the algorithm designed by Roothaan and Bagus.<sup>14</sup> For the calculation of the correlation energy, we used the well-tempered Gaussian-type functions as our basis set based upon the Roothaan–Hartree–Fock atomic orbital expansion for atoms from helium ( $Z=2$ ) to neon ( $Z=10$ ).<sup>15</sup> To compare our correlation energy with exact results, we calculated all Møller–Plesset perturbation theories (MP2, MP3, MP4), coupled cluster calculations with singles, doubles, and triples terms [CCSD(T)], and quadratic configuration interaction theories including triples terms [QCISD(T)] on GAUSSIAN 92 (Ref. 16) with the standard 6-311G\* triple zeta basis set.<sup>17</sup>

## IV. N-ELECTRON ATOMS

For  $N$ -electron atoms we can obtain the correlation energy exactly from Eq. (5) by neglecting the second term (nuclear–nuclear energy). We obtained the expression for correlation energy

$$E^{\text{corr}}(Z) \approx \frac{\partial E^{\text{HF}}}{\partial Z} \delta Z. \quad (6)$$

Using the Hellmann–Feynman theorem,

$$\frac{\partial E^{\text{HF}}}{\partial Z} = - \sum_i \left\langle \frac{1}{r_i} \right\rangle^{\text{HF}} \quad (7)$$

is just the average electron–nuclear potential energy.

TABLE II. Comparison of the dimensional renormalization correlation energies at equilibrium distances with higher level theories (all energies are in atomic units).

| $N$ | Molecule       | Term          | $R_{\text{eq}}^{\text{a}}$ | $E^{\text{corr}^{\text{b}}}$ | MP2       | MP4       | QCISD     | % Error <sup>c</sup> |
|-----|----------------|---------------|----------------------------|------------------------------|-----------|-----------|-----------|----------------------|
| 6   | BH             | $1\Sigma^+$   | 1.232                      | -0.086 03                    | -0.057 39 | -0.078 96 | -0.084 33 | -2.017 51            |
| 7   | CH             | $2\Pi$        | 1.210 1                    | -0.117 34                    | -0.080 10 | -0.103 00 | -0.107 96 | -8.688 74            |
| 8   | NH             | $3\Sigma^-$   | 1.038                      | -0.155 09                    | -0.106 34 | -0.124 12 | -0.126 97 | -22.145 11           |
| 9   | OH             | $2\Pi$        | 0.971 0                    | -0.197 91                    | -0.156 10 | -0.169 09 | -0.172 27 | -14.880 43           |
| 10  | HF             | $1\Sigma^+$   | 0.916 6                    | -0.248 61                    | -0.213 71 | -0.217 16 | -0.220 29 | -12.855 86           |
| 11  | LiO            | $2\Pi$        | 1.58                       | -0.241 20                    | -0.168 88 | -0.178 11 | -0.183 20 | -31.653 69           |
| 12  | C <sub>2</sub> | $3\Pi_u$      | 1.312 1                    | -0.233 60                    | -0.222 42 | -0.235 80 | -0.260 49 | 10.321 30            |
| 13  | BO             | $2\Sigma^+$   | 1.205                      | -0.284 75                    | -0.256 11 | -0.258 91 | -0.271 78 | -4.772 20            |
| 14  | CO             | $1\Sigma^+$   | 1.128 4                    | -0.315 12                    | -0.306 52 | -0.314 16 | -0.325 72 | 3.253 46             |
| 15  | NO             | $2\Pi$        | 1.150                      | -0.351 62                    | -0.336 85 | -0.345 50 | -0.360 61 | 2.492 28             |
| 16  | O <sub>2</sub> | $3\Sigma_g^-$ | 1.207 6                    | -0.395 23                    | -0.368 55 | -0.371 61 | -0.383 30 | -3.113 06            |
| 17  | OF             | $2\Pi$        | 1.31                       | -0.445 24                    | -0.364 72 | -0.377 88 | -0.390 37 | -14.056 21           |
| 18  | F <sub>2</sub> | $1\Sigma_g^+$ | 1.45                       | -0.494 61                    | -0.433 43 | -0.439 97 | -0.452 56 | -9.292 29            |

<sup>a</sup>In angstroms, from Ref. 24.

<sup>b</sup>Calculated from Eq. (4) in the text.

<sup>c</sup>Compared with the highest level theory [QCISD(T)].

Because both the exact and Hartree–Fock energies for all atoms is known analytically in the large- $D$  limit, we can use this limit to fix  $\delta Z$  systematically,  $\delta Z = \delta Z_{\infty}$ . The procedure has been described more thoroughly in our previous paper.<sup>10</sup> These values for  $\delta Z_{\infty}$ , which we will apply to molecules, are given in Table I, along with the electronic state and percent error when compared with exactly known energies.

For atoms with known near degeneracy mixing (beryllium, boron, and carbon), our Hartree–Fock calculations were modified to approximate the complete active valence space multiconfigurational Hartree–Fock energy,  $E^{\text{CAS}}(Z)$ . Following Davidson *et al.*,<sup>18</sup> and substituting  $E^{\text{CAS}}(Z)$  for  $E^{\text{HF}}(Z)$  in Eq. (7), we arrive at the corrected equation

$$E^{\text{corr}}(Z) \approx \frac{\partial E^{\text{HF}}}{\partial Z} \delta Z + \Delta B_1(N), \quad (8)$$

where  $\Delta B_1(N)$  has been tabulated in Ref. 18. For atoms, this renormalization procedure was shown previously to calculate the correlation energy with errors of about 20% or less relative to the exact atomic correlation energy.

## V. DIATOMIC MOLECULES

The correlation energy for molecules will have not only a charge dependency, but an internuclear distance dependency as well. With the use of Eq. (1), we assume that the leading contribution to correlation energy will lie in the  $(\partial E^{\text{HF}}/\partial Z)$  term because, at large  $R$  as well as at equilibrium,  $(\partial E^{\text{HF}}/\partial R) \approx 0$ .  $\delta Z$  is approximated to be a constant over all values of  $R$ . This allows us to fix  $\delta Z$  from the large  $R$  (atomic) limit, which we take to be the values for  $\delta Z_{\infty}$  derived from the large- $D$  limit. In this publication we are primarily concerned with correcting the Hartree–Fock theory near equilibrium. For molecules, then, we will ignore the term in Eq. (1) which takes into account the change in  $R$ ,  $\delta R$ , as a result of using the new renormalized charge.

We have calculated the correlation energy from Eq. (6) using the large- $D$  limits calculated in our previous paper and presented in Table I for several diatomic molecules. We have

included for comparison purposes higher level theories [such as MP2, MP4, and QCISD(T)] as well. All of these results are summarized in Table II at the equilibrium distance for diatomic molecules which have from  $N=6$  to 18 electrons. As can be seen in this table, we have recovered about 70% or better of the correlation energy for all molecules examined. These results are shown graphically in Fig. 1 as a plot of the correlation energy as a function of the number of electrons. This is an encouraging result, and since this has been done without modifications to  $\delta Z$  as a result of a molecular rather than atomic environment, we expect this procedure to work for all polyatomic heteronuclear and homonuclear molecules and clusters as well.

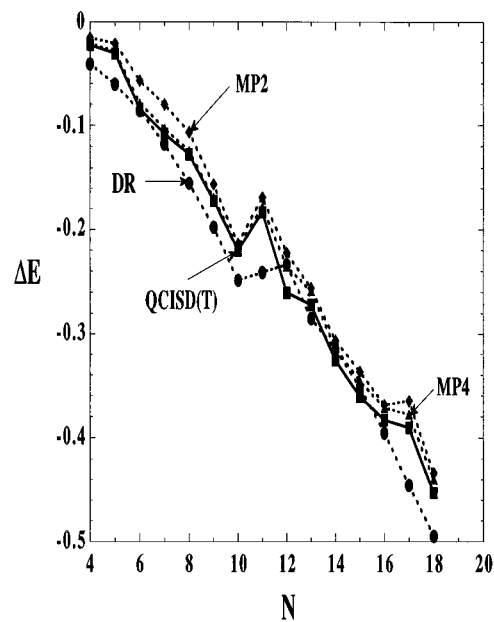


FIG. 1. Correlation energy calculated by dimensional renormalization (DR) and higher level theories [MP2, MP4, and QCISD(T)] as a function of the number of electrons in the molecule. Molecules representing each number of electrons used to generate this graph are given in Table II, except for  $N=4$  (LiH) and  $N=5$  (BeH).

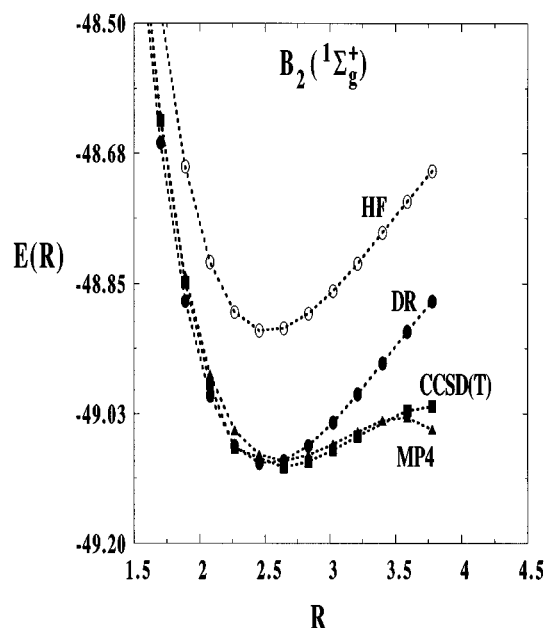


FIG. 2. Potential energy curve  $E(R)$  vs the internuclear distance  $R$  in atomic units for the  $B_2(1\Sigma_g^+)$ . In the figure, HF refers to the Hartree–Fock calculation, CCSD(T) refers to the coupled cluster calculation with singles, doubles, and triple terms, QCISD(T) refers to the quadratic configuration interaction calculation with triples terms, and MP4 refers to the Møller–Plesset perturbation calculation to the fourth order. DR refers to the dimensional renormalization procedure described in the text to correct the Hartree–Fock energy for correlation energy.

In Figs. 2–4, we present the energy curves for the homonuclear dimers  $B_2(1\Sigma_g^+)$ ,  $C_2(3\Sigma_g^+)$ , and  $F_2(1\Sigma_g^+)$ . As can be seen in these figures, our correlation energy significantly reduces the Hartree–Fock error near equilibrium, making the Hartree–Fock results comparable with the best high level

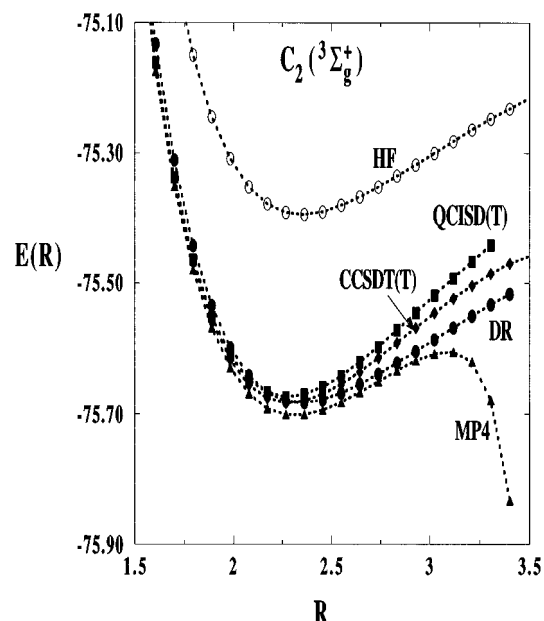


FIG. 3. Potential energy curve  $E(R)$  vs the internuclear distance  $R$  in atomic units for the  $C_2(3\Sigma)$ . The labeling in the figure is the same as in Fig. 2.

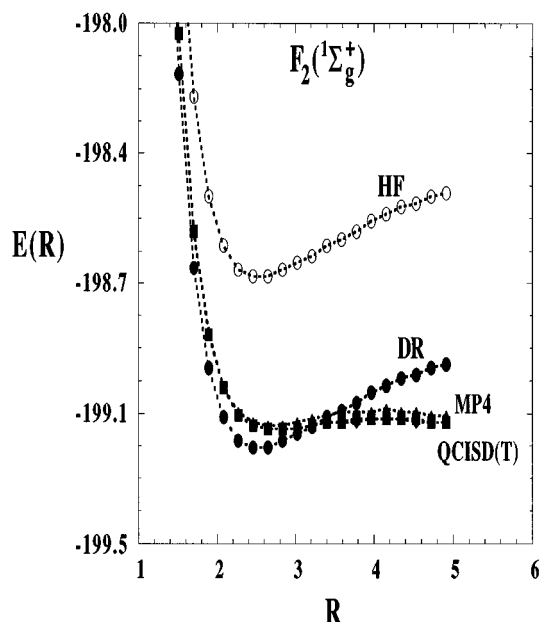


FIG. 4. Potential energy curve  $E(R)$  vs the internuclear distance  $R$  in atomic units for the  $F_2(1\Sigma_g^+)$ . The labeling in the figure is the same as in Fig. 2.

theory calculations such as QCISD(T) and CCSD(T). Because our values for  $\delta Z$  were taken systematically from the large- $D$  limit, rather than the large  $R$  dissociation limit, our energy values tend towards the Hartree–Fock limit. However, in the dissociation limit, many of the higher level theories (such as MP4) diverge. In all graphs, we present the Hartree–Fock energy curve, MP4, CCSD(T), and the QCISD(T) curve as the exact curve, as well as the dimensional renormalization curve (DR) calculated in the present work, which is the Hartree–Fock energy as a function of internuclear distance  $R$  plus our correlation energy.

The lithium dimer poses difficulties in the Hartree–Fock calculation. It has been previously noted that various electronic configurations play different roles depending upon the internuclear distance separation.<sup>19</sup> In particular, at the dissociation limit, two electronic configurations ( $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$  and  $1\sigma_g^2 1\sigma_u^2 2\sigma_u^2$ ) are significant with equal but opposite coefficients. Because of this difficulty at large  $R$ , our charge renormalization procedure cannot be expected to be as accurate as with other molecules. We found that using the large- $D$  limit for  $\delta Z$  resulted in unusually large errors. We have the option of taking a value for  $\delta Z$  from small  $R$  ( $0.5 \text{ \AA}$ ,  $\delta Z = 0.0023$ ), which we have found reduces the error of our calculated correlation energy when compared with exact correlation energy taken from QCISD(T) calculations to about 12% at equilibrium distances.

## VI. $\delta Z(R)$ AT THE LARGE- $D$ REGIME

The bulk of this work has been based upon our ability to solve for the charge renormalization parameter  $\delta Z$  in the large- $D$  limit for atoms. To solve for  $\delta Z$  as a function of  $R$ ,  $\delta Z(R)$ , it becomes necessary to be able to solve the large- $D$  limit for molecules. Although this becomes a classical prob-

lem in the large- $D$  limit, the large- $D$  solution has been solved to date only for few electron molecular systems.<sup>21</sup> For our  $N$ -particle Coulombic system with arbitrary masses,  $\{m_i\}$ , and charges,  $\{Z_i\}$ , the effective potential for  $S$  states at the large- $D$  limit has the form,<sup>22</sup>

$$V_{\text{eff}} = \sum_{i=1}^N \left[ \frac{\Gamma^i}{2m_i r_i \Gamma} + \sum_{j=i+1}^N \frac{Z_i Z_j}{(r_i^2 + r_j^2 - 2r_i r_j \gamma_{ij})^{1/2}} \right], \quad (9)$$

where the geometry of the system is defined by the radii  $\{r_i\}$

$$V_{\text{eff}} = \sum_{i=1}^4 \left\{ \frac{\Gamma^i}{2\rho_i \Gamma} - Z \left[ \frac{1}{\sqrt{\rho_i^2 + \left(z_i + \frac{1}{2}R\right)^2}} + \frac{1}{\sqrt{\rho_i^2 + \left(z_i - \frac{1}{2}R\right)^2}} \right] + \sum_{j=i+1}^4 \frac{1}{[\rho_i^2 + \rho_j^2 - 2\rho_i \rho_j \gamma_{ij} + (z_i - z_j)^2]^{1/2}} \right\} + \frac{Z^2}{R}, \quad (10)$$

where the two nuclei are located on the  $z$ -axis at  $-(R/2)$  and  $+(R/2)$ , with equal charges,  $Z$ . The  $i$ th electron is located at  $\{\rho_i, z_i\}$  and  $\gamma_{ij}$  is the cosine of the dihedral angle defined by the two electrons and the  $z$ -axis.

We begin by minimizing this potential with respect to  $\{\rho_i, z_i, \gamma_{ij}\}$  to determine the exact energy at the large- $D$  limit. Then, by setting  $\{\gamma_{ij} = 0.\}$ , we solve for  $\{\rho_i, z_i\}$  to find the Hartree–Fock energy. As we have done previously, we then varied  $\delta Z$  for a given value of  $R$  until the large- $D$  Hartree–Fock energy equaled the exact energy,

$$E_{\infty}^{\text{exact}}(R, Z) = E_{\infty}^{\text{HF}}(R, Z + \delta Z_{\infty}). \quad (11)$$

Solving Eq. (11) for all  $R$ , we find  $\delta Z_{\infty}(R)$ . We show in Fig. 5 the value of  $\delta Z_{\infty}$  as a function of  $R$ . For comparison, we

and the cosines of the interparticle angles,  $\{\gamma_{ij}\}$ . Here,  $\Gamma$  is the Gramian determinant  $|\mathbf{r}_i \cdot \mathbf{r}_j| = |\gamma_{ij}|$  for all  $N$ -particle, and  $\Gamma^i$  is the Gramian determinant for all but the  $i$ th particle.<sup>11</sup> For  $D \rightarrow \infty$ , the ground-state energy becomes a problem of finding the global minimum of this effective potential.

Following Tan and Loeser,<sup>21</sup> for the four electron diatomic molecule, the effective potential in the large- $D$  limit using  $D$ -dimensional cylindrical coordinates has form

have included  $\delta Z_3$ , which is the value for  $\delta Z$  which makes the results exact in three dimensions. This figure shows that this procedure for calculating  $\delta Z(R)$  produces a curve in qualitative agreement with the values found by using  $\delta Z(R)$  as an arbitrarily adjustable parameter, but does so in a systematic and self-consistent way. Using  $\delta Z_{\infty}$  as a function of  $R$  in a standard HF calculation results in an energy curve with a clear minimum at about 6.0 a.u. and well depth of  $-7.88 \text{ cm}^{-1}$ , as shown in Fig. 6, while exact results have shown a minimum in this curve at 5.73 a.u. with well depth  $-7.428 \text{ cm}^{-1}$ .<sup>23</sup>

## VII. DISCUSSION

Our zeroth order approximation, that  $\delta Z$  is independent of the internuclear separation distance  $R$ , does lead to some

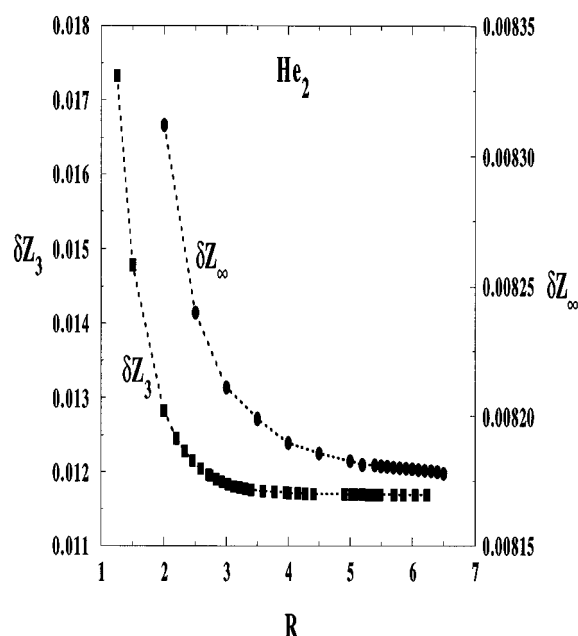


FIG. 5. Comparison of  $\delta Z_{\infty}$  and  $\delta Z_3$  as a function of internuclear separation distance  $R$  for the helium dimer.

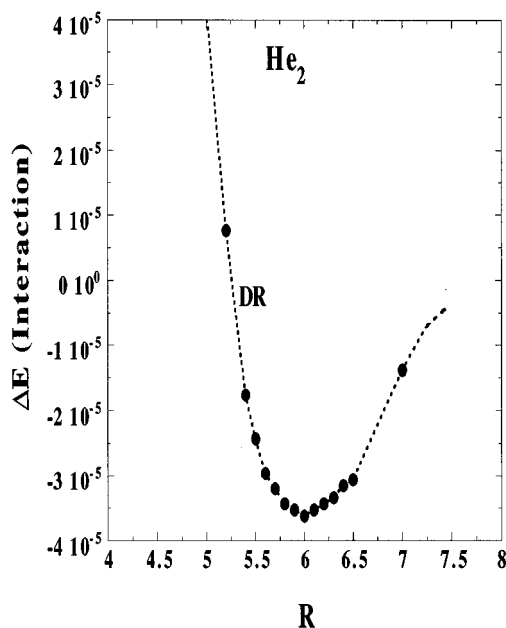


FIG. 6. Interaction potential for the helium dimer calculated from dimensional renormalization using  $\delta Z_{\infty}(R)$  as a function of internuclear distance  $R$ .

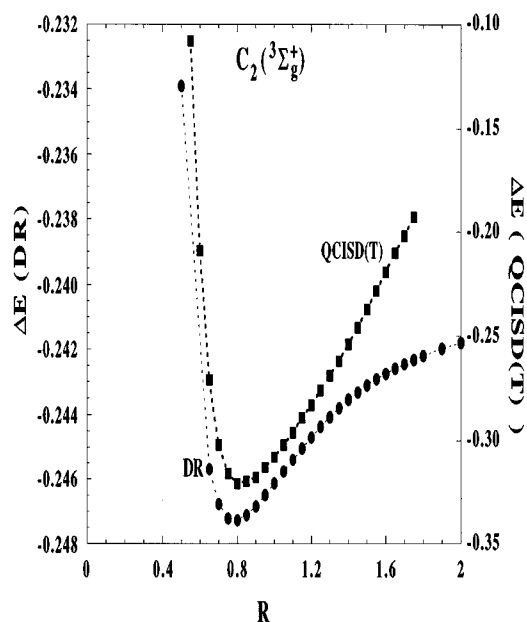


FIG. 7. Comparison of correlation energy as calculated by dimensional renormalization (DR) and QCISD(T) as a function of internuclear separation distance  $R$  for  $C_2(3\Sigma_g^+)$ .

structure of the correlation energy calculated by dimensional renormalization, as shown in Fig. 7. Here, we show that for  $C_2(3\Sigma_g^+)$ , the dimensional renormalization correlation energy behaves qualitatively in the same way that the exact correlation energy behaves [calculated from QCISD(T)]. Comparison of the two scales presented in this figure, however, demonstrates that the curvature of the DR correlation energy as a function of  $R$  is significantly less than that for the QCISD(T) correlation energy, especially near the dissociation limit.

Previous research utilizing a scaled Hartree–Fock operator has been used to define new orbitals to correct for the correlation energy of atoms and some molecules.<sup>20</sup> This method utilizes one adjustable parameter which is fixed such that the second-order Rayleigh–Schrödinger perturbation theory for the ground state vanishes, showing improved results over the original Hartree–Fock method. Although this approach was successful for the excited states of  $H_2$  molecule, the computational cost is the same as for MP2.<sup>20</sup>

One possible approach to correct the DR Correlation energy as the dissociation limit is to use the unrestricted Hartree–Fock method (UHF) instead of the restricted HF method (RHF). We have tried this approach for the  $N_2(1E_g^+)$  molecules, the results of which are given in Fig. 8. Here, we show that our correlation energy behaves in a qualitatively similar way as the correlation energy calculated from higher level theories up to the dissociation limit. Because our zeroth order approximation to the correlation energy shows only small fluctuations as a function of  $R$ , the dissociation limit correlation energy is very much a function of the behavior of the Hartree–Fock dissociation limit as demonstrated by this example. Although the use of UHF may be one approach to solving this problem, it would be best if we could find another approach to solving the large- $R$  correlation energy

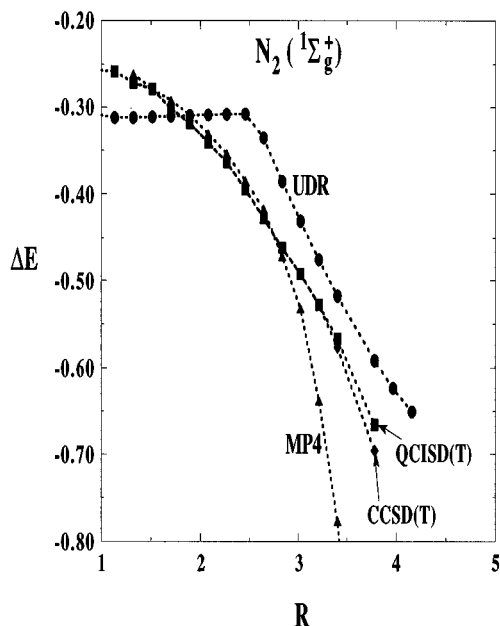


FIG. 8. Correlation energy calculated by dimensional renormalization based on unrestricted Hartree–Fock calculation (UDR) and higher level theories [MP4, CCSD(T), and QCISD(T)] as a function of the number of internuclear separation  $R$  for  $N_2(1\Sigma_g^+)$ .

based upon the renormalization procedure for solving the correlation energy at equilibrium. The approach under development is based upon the results discussed in Sec. VI of this paper.

Because we had to take no special account for the fact that we were dealing with molecules rather than atoms, we have high expectations that this procedure should work well for polyatomic molecules as well as it has for diatomic molecules. The preliminary results of the helium dimer, using the charge renormalization as a function of  $R$ , demonstrate a promising future for using a similar approach for correcting the correlation energy at the dissociation limit.

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