RICE UNIVERSITY

# PERFORMANCE COMPARISON OF CONJUGATE GRADIENT DENSITY MATRIX SEARCH AND CHEBYSHEV EXPANSION METHODS FOR AVOIDING DIAGONALIZATION IN LARGE-SCALE ELECTRONIC STRUCTURE CALCULATIONS

by

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# ABSTRACT

Performance comparison of conjugate gradient density matrix search and Chebyshev expansion methods for avoiding diagonalization in large-scale electronic structure calculations

by

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We report a performance comparison of two linear-scaling methods which avoid the diagonalization bottleneck of traditional electronic structure algorithms. The Chebyshev expansion method (CEM) is implemented for carbon tight-binding calculations of large systems and its memory and timing requirements compared to those of our previously implemented conjugate gradient density matrix search (CG-DMS). Benchmark calculations are carried out on icosahedral fullerenes from $C_{60}$ to $C_{8640}$ and the linear scaling memory and CPU requirements of CEM demonstrated. We show that the CPU requisites of CEM and CG-DMS are similar for calculations with comparable accuracy.

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# CHAPTER 1

# INTRODUCTION

Recent advances in computational quantum chemistry have introduced algorithms which scale linearly with system size by avoiding the $O(N^2)$ asymptotic scaling of the electron-electron quantum Coulomb problem,[1] introducing fast $O(N)$ quadrature schemes,[2] and replacing the diagonalization $O(N^3)$ bottleneck of traditional electronic structure methods with alternative methods.[3–16] These achievements allow theoretical chemists to address much larger chemical systems than previously possible. In this paper, we focus on the diagonalization bottleneck. Two techniques which bypass diagonalization and scale linearly with system size are the conjugate gradient-density matrix search (CG-DMS)[3–7] and the Chebyshev expansion method (CEM),[8–16] also referred as the truncated moment approach or the kernel polynomial method. In order to determine the strengths and weaknesses of these two methods, it is important to quantitatively characterize and compare their performance in calculations on chemical systems of interest.

The tight-binding (TB) method is a well-known and widely-used semi-empirical method for calculating energies and band structure of carbon systems.[17–19] TB uses a parametrized Hamiltonian and a short-range spatially-dependent potential function to replace the electron-electron Coulomb interaction. The simplicity and relative speed of the tight-binding method compared with more rigorous *ab initio* methods, such as Hartree-Fock or density-functional theory, makes it a convenient framework within which to benchmark the performance of new algorithms. Furthermore, the CPU requirements of the TB method are completely dominated by the Hamiltonian diagonalization making it an ideal candidate for benchmark calculations of algorithms that bypass this step. In this work, we have implemented the CEM algorithm within a TB scheme and compared it with our previous implementation of a competing method, CG-DMS.

The TB electronic energy is defined as

$$E_{elec} = 2 \sum_{i}^{N_{occ}} \epsilon_i,$$

where $\{\epsilon_i\}$ are the occupied eigenvalues of $H_{TB}$, $N_{occ}$ is the

number of occupied orbitals, and the prefactor 2 denotes that all electrons are paired. It is widely known that the computational time required for diagonalization of $H_{TB}$ to obtain its eigenvalues scales as $O(N^3)$ with respect to system size. This computational bottleneck prevents application of traditional electronic structure methods to truly large systems (thousands of atoms). Driven by the limited application of conventional methods, algorithms which approximate TB energies without determining the eigenvalues of $H_{TB}$ have been developed. Two important examples are CG-DMS and CEM. Instead of calculating the TB energy directly, these methods solve for the density matrix of the system. Once the density matrix has been determined, an equivalent expression of the electronic energy,

$$E_{elec} = Tr(\rho H_{TB}),$$

where $\rho$ is the density matrix of the system, can easily be solved.

In order to obtain linear-scaling with respect to system size, these methods take advantage of the inherently local nature of interactions in finite systems by implementing a spatial cutoff

beyond which interatomic interactions are disregarded. This thresholding, in addition to the local nature of the TB potential, results in sparse Hamiltonian and density matrices which are efficiently manipulated using sparse matrix routines and algorithms.[20] The sparsity seen in these calculations due to spatial thesholding results in matrix arithmetic which scales linearly with system size.[5]

In this work, we provide a comparison of the performance of linear-scaling implementations of CG-DMS and CEM within the TB method for carbon as applied to giant icosahedral fullerenes. A benchmark study of large icosahedral fullerenes using TB with CG-DMS has been reported previously.[5] Here, we perform a similar study using TB with CEM. Additionally, we draw on the CG-DMS results to compare the timing and memory requirements of CG-DMS and CEM for large carbon systems. Our results provide insight on the comparative performance of each of these methods.

# CHAPTER 2

## CONJUGATE GRADIENT DENSITY MATRIX SEARCH

All results in this work correspond to molecules with fully optimized TB geometries obtained through a molecular dynamics optimization scheme. The molecular point group symmetry was not exploited.

CG-DMS, which has been implemented in both semi-empirical[5,7] and *ab initio*[6] methods in our research group, is a variational algorithm in which the electronic energy, $E_{elec}$, is minimized as a function of the density matrix, $\rho$. Forming the derivative of $E_{elec}$ with respect to the density matrix represents the bulk of the method's computational requirements and can be expressed as[3,5]

$$\frac{\partial E_{elec}}{\partial \rho_{ij}} = 3(\rho H + H\rho)_{ji} - 2(\rho^2 H + \rho H \rho + H\rho^2)_{ji}.$$

Five matrix multiplications are required for each step of CG-DMS. A purification step[21] is used to satisfy the idempotency constraint of the density matrix, and accounts for an additional two matrix multiplications per CG-DMS step.[5] An initial guess

is required as a first approximation to the density matrix. In the TB case, this initial guess assumes half-occupation of all orbitals and no interatomic interactions. The conjugate gradient minimization algorithm[22] is then employed to iteratively minimize $E_{elec}$ with respect to the density matrix. On average, our calculations require about 15 CG iterations to converge.

In both semi-empirical and *ab initio* implementations of CG-DMS, the computational time and memory required for large scale calculations have been shown to scale linearly with system size.[5–7] The most important parameter in determining the computational cost and accuracy of CG-DMS is the spatial cutoff, $R_c$. For TB with CG-DMS, reasonably accurate results ($10^{-3}$ eV/atom) are obtained with $R_c$ = 4.0 Å.[5] Based on these results, all CG-DMS and CEM calculations reported in this work utilize a 4.0 Å spatial threshold.

# CHAPTER 3

## THE CHEBYSHEV EXPANSION METHOD

In contrast to CG-DMS, CEM calculates the density matrix of a system directly using only $H_{TB}$ and a Fermi-Dirac distribution for the electronic occupations. In this work we follow the formalism introduced previously by Goedecker and Teter.[13] We define the electronic density matrix as a polynomial expansion of $H_{TB}$ scaled such that its eigenvalues fall between -1 and 1. This relationship can be expressed as

$$\rho = f\left(\frac{\overline{H} - \mu}{kT}\right),$$

where $f$ represents the Fermi-Dirac distribution, $\mu$ is the chemical potential, $k$ is Boltzmann's constant, T is the absolute temperature of the system, and $\overline{H}$ is the scaled $H_{TB}$. $\overline{H}$ is determined by calculating the largest and smallest eigenvalues of $H_{TB}$ via a linear-scaling Lanczos method.[23] $\mu$ is determined by enforcing the electron count of the system,

$$N_{elec} = Tr(\rho),$$

where $N_{elec}$ is the total number of electrons in the system. Using Newton's approximation, we achieve rapid and tight convergence to the Fermi level of the system. The accuracy of $\mu$ determines the accuracy of the Fermi-Dirac distribution, which in turn is used to calculate the Chebyshev coefficients used in the expansion of $\overline{H}$. The central expression which must be solved in CEM for orthogonal electronic-structure calculations can be written as

$$\rho = c_0 + \sum_{i=1}^{CPO} c_i T_i$$

where $\{c_i\}$ are the Chebyshev coefficients derived from the Fermi-Dirac distribution, $\{T_i\}$ are the Chebyshev recursion relations of the scaled Hamiltonian, as defined elsewhere[13], and $CPO$ is the Chebyshev polynomial order. A formalism for non-orthogonal cases has been developed separately.[15] The $CPO$ determines the accuracy of the density matrix approximation, where larger values of $CPO$ result in increasing accuracy. The number of matrix multiplications required in CEM is equal to the order of the expansion. We find that $\rho$ is sufficiently idempotent for the accuracy required for our calculations, and that

no purification step is normally necessary.

In our implementation of CEM, we use the above definition to calculate the density matrix of our system directly from $H_{TB}$. While we impose a set 4.0 Å spatial threshold in our implementation of CEM, a method which exploits the widening column vectors of $\{T_i\}$ with increasing CPO has recently been reported.[16] However, a complete discussion and comparison of this method with other linear-scaling techniques has yet to be published. As reported by other authors,[16] we also greatly increase the efficiency of the Fermi level determination by calculating and storing the column vectors of the recursion matrices $\{T_i\}$ outside the Newton-Rapson loop. This calculation is independent of the method by which the Hamiltonian is derived, and therefore applies broadly to most semi-empirical and *ab initio* quantum chemical methods. CEM has been implemented in both TB[8–10] and DFT methods.[12] Furthermore, CEM has been implemented to solve for second order properties of materials, including optical-absorbtion spectra and the density of states.[11]

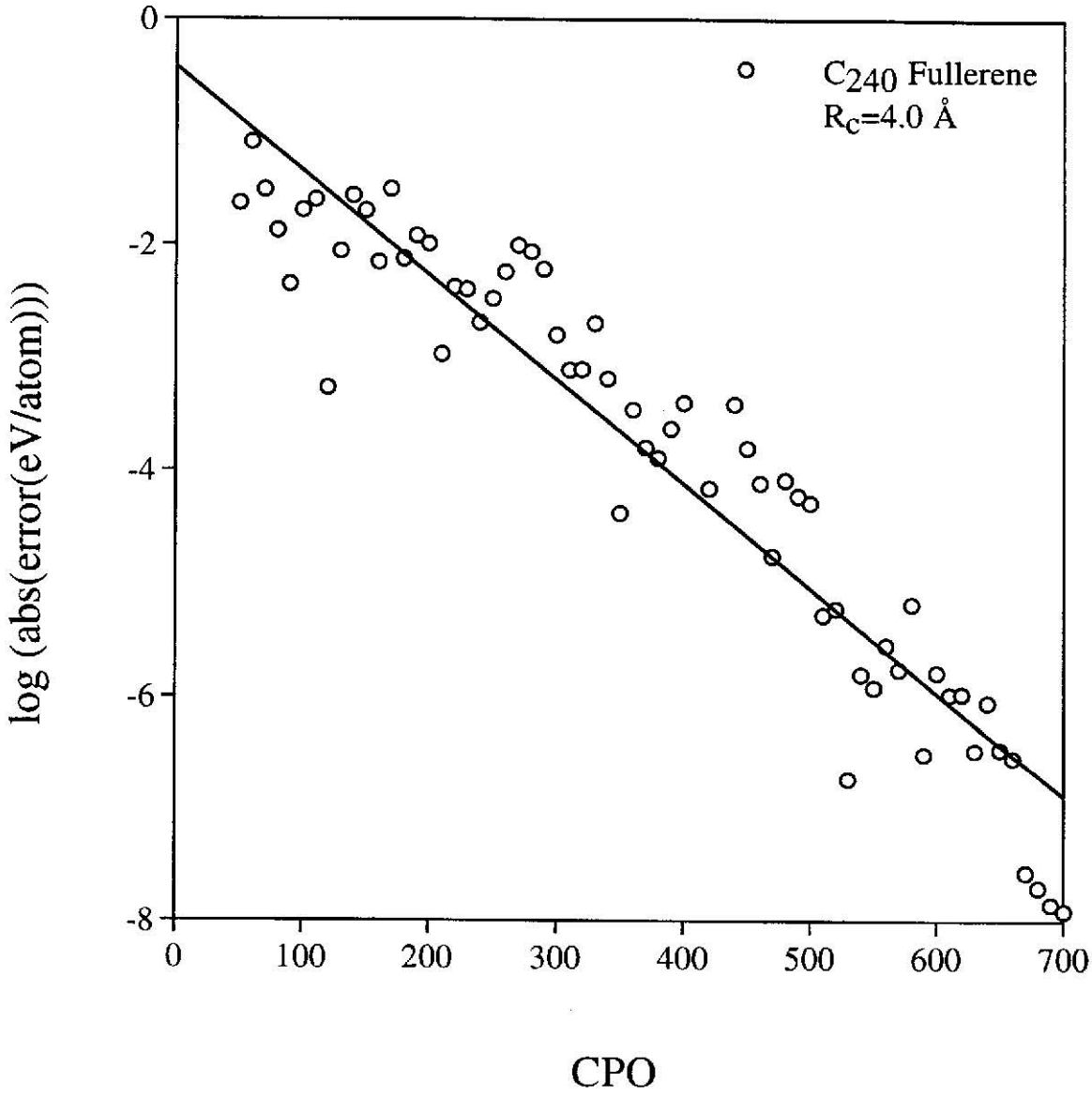
# CHAPTER 4

## PERFORMANCE COMPARISON OF CG-DMS AND CEM

Before comparing the timing characteristics of CG-DMS and CEM, it is important to establish the conditions under which the methods provide similar degrees of accuracy for large fullerenes. As mentioned before, previous work has demonstrated that the accuracy of linear-scaling CG-DMS calculations depends strongly on the cutoff radius, $R_c$, and that $R_c$ = 4.0 Å attains a reasonable compromise between accuracy and computational requirements.[5] For simplicity, we perform all calculations in this work using this cutoff radius.

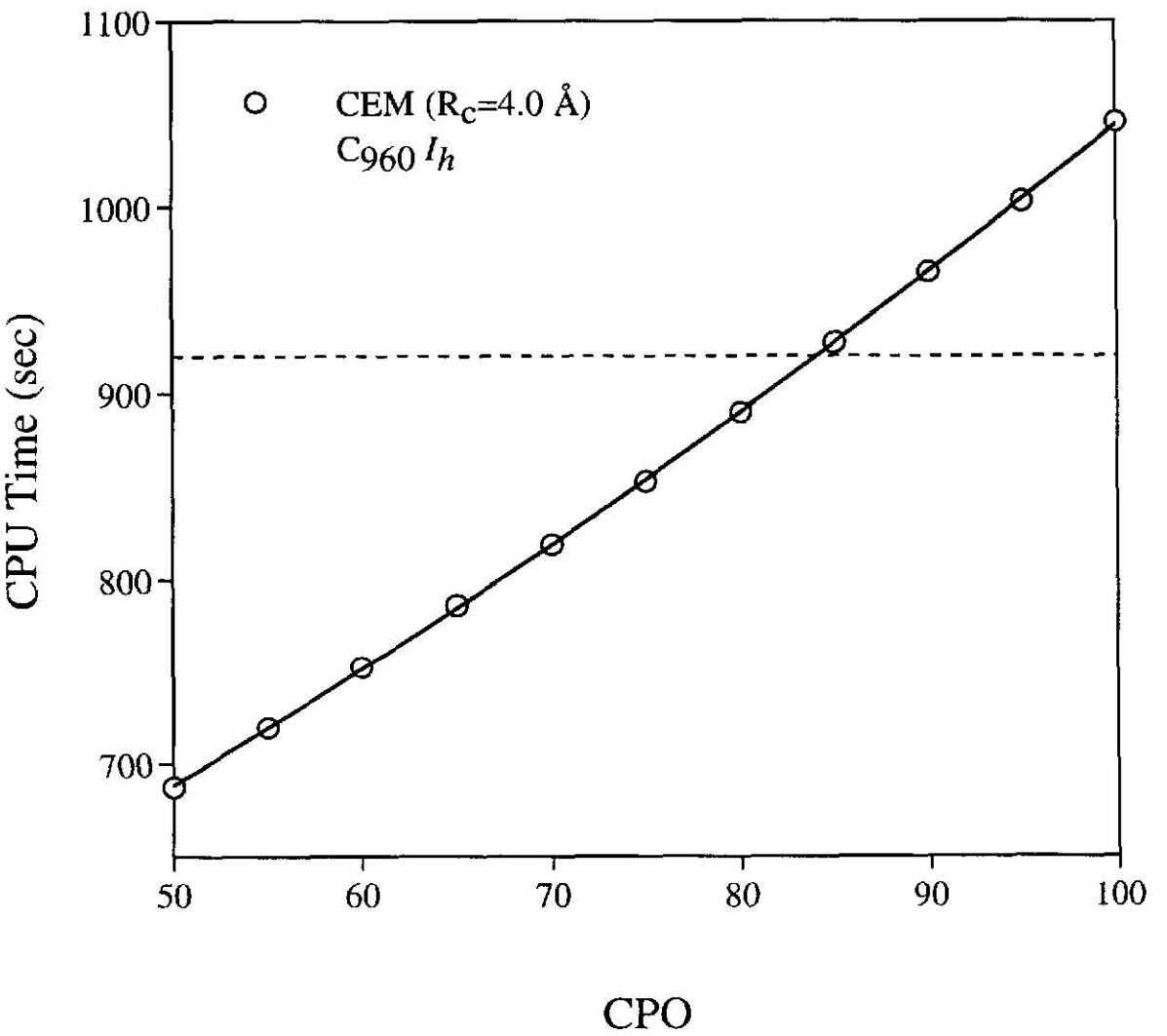
In addition to spatial thresholding, the accuracy of the CEM method depends strongly on the accuracy of the Chebyshev expansion, which depends mainly on the $CPO$. In Figure 1, we show absolute error of our energy calculations in eV per atom as a function of $CPO$ for the icosahedral fullerene $C_{240}$, or $C_{240}$ $I_h$. Our results show an exponential convergence to the exact energy with increasing $CPO$, a result predicted by theory.[14]

Figure 1. Log of the absolute error in eV per atom of CEM calculations on the icosahedral fullerene $C_{240}$ as a function of the Chebyshev polynomial order.



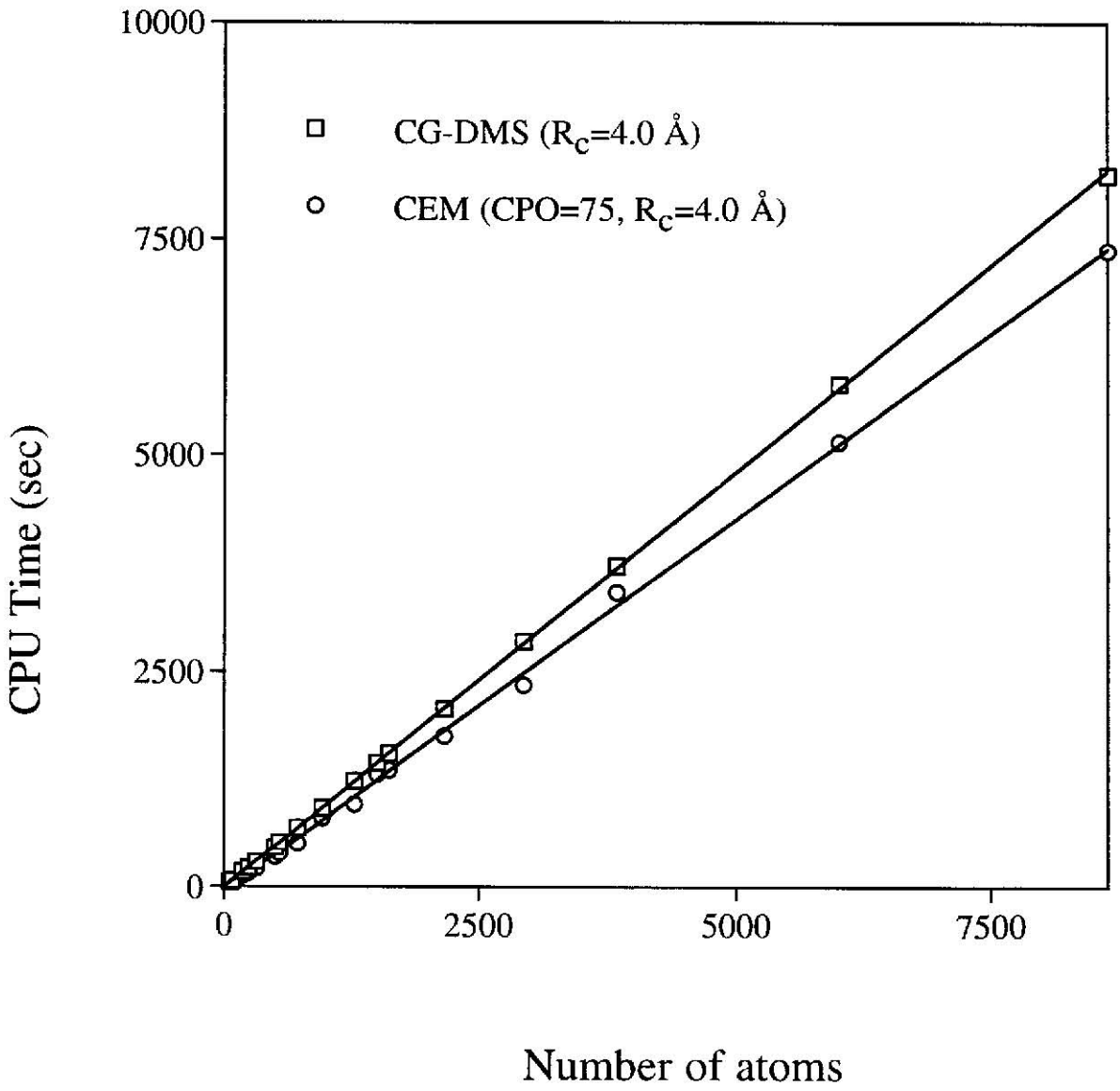
In Figure 2, we show the CPU time of CEM calculations on $C_{960}$ $I_h$ with respect to the $CPO$. The results clearly show a linear relationship between CPU time and $CPO$ for CEM calculations, with the best-fit line for the log-log plot of these points having a slope of 2.04. Additionally, it is shown that the CPU time required for a CEM calculation on $C_{960}$ $I_h$ crosses over with CG-DMS (the dotted line) at CPO $\approx$ 85. Based on the results from Figures 1 and 2, we must establish a $CPO$ which achieves the appropriate accuracy with minimal CPU requirements. From the results shown in Figure 1, we find that $CPO$=75 is adequate to achieve an accuracy of approximately $10^{-3}$ eV per atom without requiring excessive computational time.

Figure 2. Plot depicting computational time requirements as a function of Chebyshev polynomial order (CPO) for CEM calculations on the icosahedral fullerene $C_{960}$. Dotted line represents the CPU time required for a CG-DMS calculation on $C_{960}$.



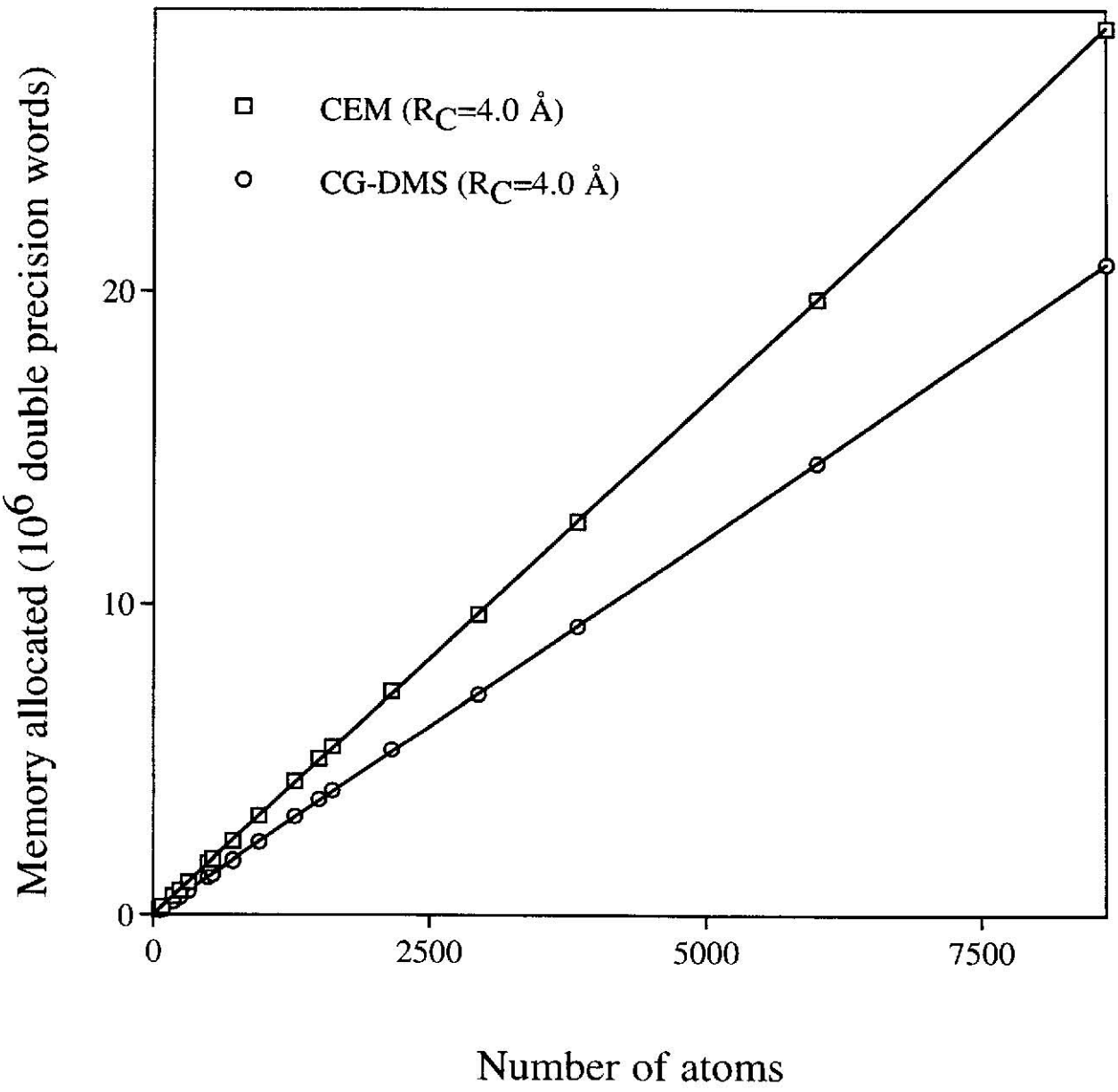
While the computational scaling properties of TB with CG-DMS as applied to systems containing thousands of atoms have been discussed elsewhere,[5] analogous results for CEM have not been reported to date. In Figure 3, we show the CPU time required for CG-DMS and CEM calculations with $CPO = 75$ and $R_c$=4.0 Å as a function of system size for fullerenes up to 8640 atoms. Clearly, CPU times scale linearly with system size in our implementation of CEM as well as CG-DMS. Additionally, CEM requires about 10 percent less CPU time than CG-DMS in these calculations.

Figure 3. CPU time for CEM calculations on icosahedral fullerenes up to 8640 atoms.



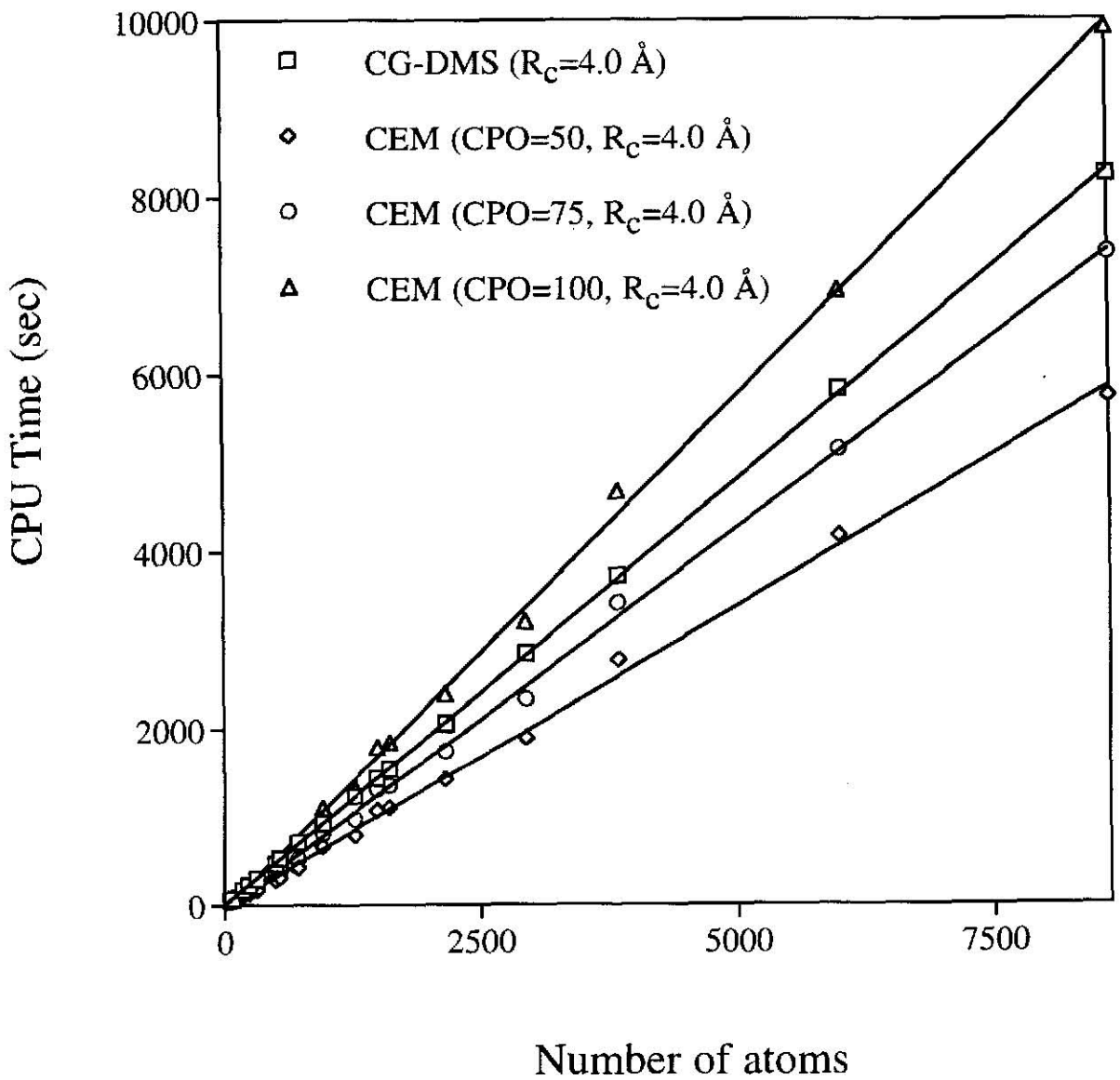
In Figure 4, we compare the memory requirements of CG-DMS and CEM for calculations on giant icosahedral fullerenes up to 8640 atoms. Again, we see that the memory requirements of our calculations scale linearly with system size. Additionally, we show that our implementation of CEM requires slightly more memory than CG-DMS. The memory required for our implementation of CEM is dependent on both the $CPO$ and the $R_c$.

Figure 4. Memory required in millions of double precision words for CG-DMS and CEM calculations on icosahedral fullerenes up to 8640 atoms.



In Figure 5, we show a comparison in the CPU time required to perform each of the calculations shown in Figure 3. This plot compares CG-DMS and CEM with $R_c$=4.0 Å and $CPO$ equal to 50, 75, and 100. Our results confirm those shown in Figure 2. CEM calculations with $CPO$ equal to 50 and 75 require less CPU time than CG-DMS calculations while CEM calculations with $CPO$=100 require more CPU time than CG-DMS calculations.

Figure 5. CPU time of CG-DMS and CEM calculations on icosahedral fullerenes up to 8640 atoms for $CPO$ equal to 50, 75, and 100.



# CHAPTER 5

# CONCLUSIONS

In this work we provide a comparison of two competing methods of performing TB electronic-structure calculations in which the computational time and memory scale linearly with system size. Our results show that CEM calculations on large systems are slightly faster than CG-DMS calculations of similar accuracy while requiring slightly more memory. Based on these results, CEM is shown to be an efficient linear-scaling technique for avoiding the diagonalization bottleneck of traditional TB methods. The computational requirements of CEM compare favorably with CG-DMS, suggesting the importance of future implementations of CEM into semi-empirical and *ab initio* quantum chemical methods.

# REFERENCES

1. M.C. Strain, G.E. Scuseria, and M.J. Frisch, Science **271**, 51 (1996).

2. R.E. Stratmann, G.E. Scuseria, and M.J. Frisch, Chem. Phys. Lett. **257**, 213 (1996).

3. X.-P. Li, W. Nunes, and D. Vanderbilt, Phys. Rev. B **47**, 10891 (1993).

4. M.S. Daw, Phys. Rev. B **47**, 10895 (1993).

5. C.H. Xu and G.E. Scuseria, Chem. Phys. Lett. **262**, 219 (1996).

6. J.M. Millam and G.E. Scuseria, J. Chem. Phys. **106**, 5569 (1997).

7. A.D. Daniels, J.M. Millam, and G.E. Scuseria, J. Chem. Phys. **107**, 425 (1997).

8. L.W. Wang and A. Zunger, J. Chem. Phys. **100**, 2394 (1994).

9. R.N. Silver and H. Roder, Int. J. Mod. Phys. **5**, 735 (1994).

10. S. Goedecker and L. Colombo, Phys. Rev. Lett. **73**, 122 (1994).

11. L-W Wang, Phys. Rev. B **49**, 10154 (1994).

12. Y. Huang, D.J. Kouri, and D.K. Hoffman, Chem. Phys. Lett. **243**, 367 (1995).

13. S. Goedecker and M. Teter, Phys. Rev. B **51**, 9455 (1995).

14. D.J. Kouri, Y. Huang, D.J. Hoffman, J. Phys. Chem. **100**, 7903 (1996).

15. H. Roder, R.N. Silver, D.A. Drabold, and J.J. Dong, Phys. Rev. B **55**, 15382 (1997).

16. R. Baer and M. Head-Gordon, J. Chem. Phys. **107**, 10003 (1997).

17. C.-H. Xu, C.Z. Wang, C.T. Chan, and K.M. Ho, J. Phys. Condens. Matter **4**, 6047 (1992).

18. S -Y. Qiu, C.Z. Wang, K.M. Ho, and C.T. Chan, J. Phys. Condens. Matter **6**, 9153 (1994).

19. C.M. Goringe, D.R. Bowler, and E. Hernandez, Rep. Prog. Phys. **60**, 1447 (1997).

20. S. Pissanetsky, Sparse Matrix Technology (Academic Press, 1984).

21. R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).

22. W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P.

Flannery, Numerical Recipes in Fortran, 2nd Ed. (Cambridge University Press, 1992).

23. B.N. Bartlett, The Symmetric Eigenvalue Problem (Prentice-Hall, Englewood Cliffs, NJ, 1980).