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Renormalization group approach for electronic excitations in atoms

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Abstract

We present a finite size numerical renormalization group approach to obtain low-lying electronic excitations in atoms and molecules. Results show that the method is reasonably accurate for estimating the electronic excitations for carbon and silicon atoms. The method is general and has potential applicability for molecular systems. © 1998. Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The self-consistent field (SCF) approximation, which is based on the idea that we can approximately describe an interacting fermion system in terms of an effective single-particle model, remains the major approach for quantitative calculations for large systems. There are mainly two different kinds of SCF approaches for electronic structure calculations: the Hartree–Fock (HF) approximation and the Kohn–Sham (KS) method, which is the basis for modern density functional theory. The HF approximation treats the exchange energy exactly but ignores correlation, while in the KS approach formally both the exchange and correlation energies are included but in practice the exact functional form of the exchange correlation potential is yet unknown.

The HF approximation usually yields good zeroth order approximation results for the ground state and in the asymptotic limit of large molecules scales approximately as N^2, where N is the number of basis functions involved in the calculation. Recently, much effort has been made in the development of linear scaling quantum calculations [1,2]. Recovering the remaining error in the total energy, the correlation energy, is the main driving force for introducing new methods for calculating electronic structure. A wide variety of techniques are currently available for predicting accurate correlation energies, including configuration interaction (CI), many-body perturbation theory (MP2, MP3, MP4, etc.), multi-configuration Hartree–Fock (MCSCF), coupled cluster methods (CC) [3] electron propagator methods [4], quantum Monte Carlo [5], dimensional scaling [6] and density functional methods [7,8].

A variety of methods have been previously proposed to introduce correlation energy in HF calculations. Examples include the g-Hartree approach [9], the soft-Coulomb hole effective interaction [10] and dimensional renormalization [11]. All these approaches, however, fall under the same generalization of finding an effective Hamiltonian such that the eigenvalues of the effective Hamiltonian approaches the exact Hamiltonian eigenvalues [12]. Freed and

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co-workers have developed the ab initio effective valence shell Hamiltonian method, a fully correlated ab initio many-body perturbation method which also produces the true forms of the effective Hamiltonians that are modeled by semiempirical methods. This approach was applied with very good results for atoms and molecules [13].

While there are numerous highly successful methods for obtaining the ground state energies, a reliable method for obtaining the low-lying excited states is one of the major outstanding problems of quantum chemistry. This study will attempt to use the numerical renormalization group (RG) approach which has been developed recently by one of us [14,15], for interacting finite Fermi systems, to treat electronic excitations. This new RG approach which takes into account the correlation effects is used in this letter to obtain low-lying electronic excitations in atoms. As examples, we present detailed calculations for carbon and silicon atoms. The method is general and can be applied to molecular systems.

2. Renormalization group approach

In the RG method developed by Wilson [16,17], states above a certain energy, called the ‘‘cutoff’’ energy Λ, are removed from the theory, and the Hamiltonian is modified to produce the same results for all physical measurements that involve the remaining modes. This procedure is called ‘‘integrating out the high-energy states’’, a terminology based on the path-integral representation of statistical mechanics. The parameters that specify the different interaction strengths in the Hamiltonian change (‘‘flow’’) as Λ is reduced. Some interaction strengths flow to zero and are thus unimportant for the low-energy description, these are called irrelevant, while others remain important in the low-energy effective theory. The RG has been applied with enormous success to classical statistical mechanical systems undergoing second-order phase transitions. It has only recently become possible, due to a combination of theoretical and computational advances, to apply the RG method to systems containing many electrons.

The difference between classical phase transitions and electronic problems lies in the fact that the low-energy and long-distance behavior of phase transitions is governed by only a few relevant variables, which makes it easy to keep track of the effective interactions. However, an accurate treatment of the electronic problem requires us to keep track of all low-energy four-point interactions. A formalism for treating electronic systems using RG has recently been developed by Shankar [18]. Based on this general formalism, a numerical RG method has been developed recently by one of us [14,15] to analyze the electronic properties of clusters. The heart of the RG method is to find the best possible effective description of the system at every energy scale (especially low energies), in terms of effective single-particle energies and effective interactions.

Let us now turn to the concrete details of the implementation of this program.

In this study we start by separating the Hamiltonian into a Hartree–Fock part H_0 and a part that involves residual electronic interactions V. The RG program consists of the following well-defined steps [14,15]: (1) Diagonalize H_0 to get the single-particle energies ϵ_α and wave-functions $\psi_\alpha(\boldsymbol{r})$, (2) Reexpress the full Hamiltonian in terms of these single particle levels. The Hamiltonian now looks like

$$H = \sum_{\alpha,s} \epsilon_\alpha c^\dagger_{\alpha,s} c_{\alpha,s} + \sum_{\alpha\beta\gamma\delta,ss'} V_{\alpha\beta\gamma\delta,ss'} c^\dagger_{\alpha,s} c^\dagger_{\beta,s'} c_{\gamma,s'} c_{\delta,s} \tag{1}$$

where $c_{\alpha,s}$ and $c^\dagger_{\alpha,s}$ represent the annihilation and creation operators for the state α with spin s and the $V_{\alpha\beta\gamma\delta,ss'}$ are the matrix elements of the two-body interaction. (3) Now we start integrating out the high-energy states one by one. We end up with a new effective Hamiltonian, and finally: (4) Just repeat the step for the next highest energy and continue till all the states have been integrated. Note that high-energy excitations can occur from occupied states far below the HOMO or to unoccupied states far above the HOMO. The operational difference between RG and perturbation theory [19] is that the corrected matrix elements $V'_{\alpha\beta\gamma\delta,ss'}$, rather than the original matrix elements, are used in subsequent steps. (5) The third-order RG approach presented here has an important internal validity criterion. At any stage of the calculation, one can check the ratio of the third-order to second-order contributions to the LUMO energies and interactions. If this ratio is small, it indicates that renormalized perturbation theory converges well, and we can expect the errors to be small. However if this ratio approaches 1 then we can expect all orders in renormalized perturbation theory to contribute equally, and the entire scheme breaks down.

It turns out to be most convenient to compute the perturbative corrections in a path-integral formulation. The reason is that once a state has been integrated out the problem is, strictly speaking, no longer Hamiltonian. One is forced to introduce interactions nonlocal in time between the remaining states. One then starts with the partition function of the original Hamiltonian problem and converts it in the standard way to a Grassmann path integral [18]

$$Z=\mathrm{Tr}[\exp-\beta H]=\int D\bar{\eta}_{\alpha,s}D\eta_{\alpha,s}\exp\int_0^{\beta}d\tau \times\left(\sum_{\alpha,s}\bar{\eta}_{\alpha,s}\frac{\partial}{\partial\tau}\eta_{\alpha,s}-H[\bar{\eta}_{\alpha,s},\eta_{\alpha,s}]\right) \tag{2}$$

where β stands for the inverse temperature (taken to ∞ at the end of the computation to recover ground state properties). The $\bar{\eta}_{\alpha,s}$ and $\eta_{\alpha,s}$ are anticommuting Grassmann numbers corresponding to $c^{\dagger}_{\alpha,s}$ and $c_{\alpha,s}$. A new quantity z, the wave-function renormalization, makes its appearance when states are integrated out. This corresponds to the overlap of the true eigenstates with the single-particle-like states. The flow of z is also kept track of as Λ decreases. Path-integral perturbation theory is standard and has a one-to-one correspondence with the usual Hamiltonian perturbation approaches.

This novel RG technique has been tested with excellent results for chains [20,14] and two clusters, C_{12} [21,14] and C_{60} [15] using H_0 the tight-binding Hamiltonian.

3. Applications for electronic excitations in atoms

To illustrate the application of the RG technique to electronic structure of atoms, we compute the low excitations for carbon and silicon atoms. In order to carry out the RG procedure, we started with the HF basis set for the two atoms. In the HF structure for the neutral atoms, the partially full p level gets energetically split between the full and the empty states, and the symmetry is lost. To retain the symmetry, we started with the HF solution for the closed-shell doubly ionized atoms, C^{2+} and Si^{2+}. For C^{2+}, we used the Double-Zeta basis set of $(9s,5p)$ contracted to $[4s,2p]$ [24], while for Si^{2+} we used a Double-Zeta basis set of $(11s,7p)$ contracted to $[6s,4p]$ [24]. The matrix elements of the two-body Coulomb interaction were obtained from the Gaussian92 [25] program. We then added two electrons into the lowest unoccupied molecular orbital (LUMO), and obtained the RG-improved effective single-particle energies, interactions and wave functions renormalizations z. In this context it is important that for two particles propagating in the LUMO, there is a two-body composite operator wave function renormalization z_2 which is distinct from the single-particle z.

Now one carries out the following steps: (i) order the different single particle states such that states farthest from the LUMO are integrated first. For example, in our HF calculation for C^{2+}, the states with their energies in atomic units were $\epsilon_{1s}=-12.65$, $\epsilon_{2s}=-1.69$, $\epsilon_{2p}=-0.86$, $\epsilon_{3p}=-0.20$, $\epsilon_{3s}=-0.14$, $\epsilon_{4s}=22.34$. States $1s$ and $2s$ are occupied, while the others are empty. $2p$ is the LUMO, and we set the chemical potential μ exactly at ϵ_{2p}. Based on the energies we chose the order of integration to be $4s$, $1s$, $2s$, $3s$, $3p$, $2p$, (ii) now we start integrating out the high-energy states using the standard rules of path-integral diagrammatics. Let us call the state currently being integrated out h (to denote high energy) and as the yet unintegrated states l. We separate the action as $S=S_h+S_l+S_i$, where S_i is the coupling between the low and high energy sectors. We perform the Grassman integration of $\bar{\eta}_h\eta_h$ by taking recourse to the cumulant expansion

$$\langle\exp S_i\rangle=\exp\{\langle S_i\rangle+\tfrac{1}{2}\langle S_i^2\rangle_c+\tfrac{1}{6}\langle S_i^3\rangle_c+\cdots\} \tag{3}$$

where all averages are taken in the ensemble of h, the subscript c means connected diagrams, and we go to third order in S_i. We have generated a new effective action for the low energy sector, which implies new effective single-particle energies, quasiparticle residues and matrix elements. As an example, consider the first nontrivial self-energy correction, the sunrise diagram [22,23]. The formulas for the corrections to the energy ϵ_α and z_α are

$$\delta\epsilon_\alpha = \frac{V_{\alpha\beta\gamma\delta}^{(n_{\min}-1)} V_{\delta\gamma\beta\alpha}^{(n_{\min}-1)}}{\left(z_\beta^{(n_\beta-1)} z_\gamma^{(n_\gamma-1)} z_\delta^{(n_\delta-1)} \right)^{-1}}$$

$$\frac{N_\beta(1-N_\gamma)(1-N_\delta) + (1-N_\beta) N_\gamma N_\delta}{\epsilon_\alpha + \epsilon_\beta^{(n_\beta-1)} - \epsilon_\gamma^{(n_\gamma-1)} - \epsilon_\delta^{(n_\delta-1)}}$$

$$\delta(z_\alpha)^{-1} = \frac{V_{\alpha\beta\gamma\delta}^{(n_{\min}-1)} V_{\delta\gamma\beta\alpha}^{(n_{\min}-1)}}{\left(z_\beta^{(n_\beta-1)} z_\gamma^{(n_\gamma-1)} z_\delta^{(n_\delta-1)} \right)^{-1}}$$

$$\frac{N_\beta(1-N_\gamma)(1-N_\delta) + (1-N_\beta) N_\gamma N_\delta}{\left(\epsilon_\alpha + \epsilon_\beta^{(n_\beta-1)} - \epsilon_\gamma^{(n_\gamma-1)} - \epsilon_\delta^{(n_\delta-1)} \right)^2} \qquad (4)$$

The internal lines $(\beta\gamma\delta)$ range over all previously integrated levels. Note the important point is that the most recent renormalized values are used for the matrix elements, energies and z. For example, n_β refers to the RG step at which β was integrated out (thus making $\epsilon_\beta^{(n_\beta-1)}$ the most recent value of its energy) and $n_{\min} = \min(n_\beta, n_\gamma, n_\delta)$, (iii) repeat the step for the next highest energy and continue till all the states have been integrated. To repeat, the operational difference between this perturbative RG and naive perturbative methods [19] is that the corrected matrix elements, rather than the original matrix elements, are used in subsequent steps. This corresponds to summing all third-order skeleton graphs for the interaction, and all second-order skeleton graphs for the single particle energy and z, and finally (iv) in order to find the energy of two electrons in the LUMO, we look for the poles of the two-body propagator. This involves the additional computation of the wave function renormalization z_2 of the composite operator.

We find that the validity criterion of RG is well satisfied: The ratio of third-order to second-order for the LUMO matrix elements never exceeds 0.22. For both atoms, we obtain the correct order of ground and excited states. Table 1 compares the experimental number [26] for the splitting between the ground state and the first excited state with the results of different calculational schemes, including basis set reduction (BSR) [27,28], Hartree–Fock (HF) (V. Staemmler, private communication), Configuration Interaction with Single and Double excitations (CISD) (V. Staemmler, private communication) and Coupled Clusters with Single and Double Excitations (CCSD) (V. Staemmler, private communication). Furthermore, the ionization potentials are reproduced with remarkable accuracy, the experimental numbers being 11.26 eV (carbon) and 8.15 eV (silicon) [26], with the RG producing 11.51 eV and 8.15 eV respectively. The RG is expected to get better as system size increases (recall that it gives exact answers for low-energy long-distance correlations functions for macroscopic systems undergoing critical phenomena [16,17]), while purely perturbative methods are expected to get worse. Higher angular momentum states are not included in the calculations, since they are not present in the basis set. However, more than single and double excitations are included (in the third-order diagrams), and so as expected the RG results are better than CCSD with the same basis set. While results for carbon with larger basis set have been available for some time [29], comparable results for silicon are lacking. If we included higher angular momentum states, or in general a larger basis set, we would obtain better results. However, our goal is not to obtain the best possible results for carbon, but to show the feasibility and general applicability of the method.

Table 1
Comparison of different calculational schemes for the splitting between the ground state and the first excited state for carbon and silicon atoms

System	Expt.	RG	BSR	HF	CISD	CCSD
C: $^3P \to {}^1D$	1.26	1.11	1.20	1.55	1.50	1.50
Si: $^3P \to {}^1D$	0.78	0.87	1.72	1.08	1.04	1.04

All energies are in eV.

4. Discussion

The advantages of RG over other approximation schemes can be summarized as follows: (i) RG takes systematic account of the contributions of higher energy states to processes happening at low energies. We start integrating out the highest energy states first because they are expected to have the least effect on the low-energy states. However, they have a significant effect on the states close to them, and RG allows these effects to propagate to the lowest states. (ii) RG can handle degeneracies easily. In fact, all the cases to which the RG technique has been applied [14,15] have ground state degeneracies due to a partially filled HOMO and the new technique specifies the correct ground state due to residual electronic interactions. (iii) Excited state properties can be obtained by stopping the RG process before all states are integrated out. One obtains an effective theory of the lowest few states, which can be solved to obtain excited state energies, oscillator strengths etc. (iv) Third-order RG contains an internal validity criterion. At each RG step one compares the third order correction to the second order one. As long as this ratio is small the perturbative RG is well behaved. In RG one does not have to do extra work to determine the validity of the approximation. In order to obtain a similar criterion for CISD or CCSD, one would have to do another calculation which takes triple excitations into account to determine the error. (v) Finite-temperature calculations are a trivial extension of the method described above, with frequency integrations in diagrams being replaced by Matsubara sums [22,23]. To obtain results in a $\boldsymbol{E}$ or a $\boldsymbol{B}$ field [30], one can either carry out the calculations by modifying the energy eigenstates, or by computing response functions in the unperturbed system.

Finally, it is appropriate to discuss the relationship of this RG method to other RG approaches for electronic structure. The first such approach used a mesh in real space [31] and the idea of real-space RG (coarse-graining the mesh) but proved to be computationally expensive. Recently, White has developed the density matrix RG [32], which works excellently in one-dimensional condensed Fermi systems, but is computationally prohibitive in two or higher dimensions. Since this again contains the idea of piecing together identical subunits, it is unclear how it is to be applied to atoms (however, it could be applied to chains of identical atoms very easily). There has also been work on BSR using a threshold criterion for matrix elements, and treating the effect of the neglected states variationally [33], which produces very good results. Most recently, a beautiful adaptive RG technique has been developed which could be applied to systems in any dimension [34], in which a basis set is chosen so as to make the two-body interaction matrix elements between the high- and low-energy subspaces small. However, to our knowledge, this has not been applied to chemical systems.

Finally, the RG, like MP perturbation calculations, is a polynomial-time algorithm. Without taking account of symmetries the computation time goes as N^8, which is very high. In practice, however, symmetries (such as the conservation of angular momentum and parity) enormously reduce the number of matrix elements to be recomputed. The C_{60} (60 interacting π-electrons) computation [15] took one hour on an SGI workstation. Carbon and silicon take less than a minute each. These are extremely encouraging results and give us hope that the finite size RG method may turn out to be very useful in analyzing low-lying excitations for atoms and molecules.

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