INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **34** (2001) L401–L407 www.iop.org/Journals/jb PII: S0953-4075(01)24307-7

LETTER TO THE EDITOR

A classical mechanics technique for quantum linear response

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Received 26 April 2001

Abstract

It is shown that the lowest random phase approximation (RPA) excitation energies of a quantum many-fermion system can be obtained by minimizing an effective classical energy functional. The idea is based on an analogy between the RPA and classical Hamiltonian equations of motion. Generalized Lanczos recursion allows the minimum to be found very efficiently. The technique is used to find the electronic excitation spectrum of the C_{60} molecule.

The random phase approximation (RPA) is central to the theory of excitations in correlated many-particle systems [1, 2]. It is widely used to describe correlation effects in the linear response of nuclei [3, 4], atoms [5, 6], molecules [7–10], nanoclusters [11, 12], semiconductor quantum dots [13], quantum wells [14] and bulk materials [15]. Large systems of RPA-type equations are of particular significance in the photochemistry of biological molecules, which is governed by the configuration of excited-state adiabatic surfaces [16, 17].

RPA excitation energies are obtained as the eigenvalues of a non-Hermitian matrix [3],

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \tag{1}$$

which I assume to be real for simplicity. The $N \times N$ symmetric matrices A and B describe particle–particle interactions. Their matrix elements are simple combinations of the two-particle interaction matrix elements of the Hamiltonian in the basis of Hartree–Fock (HF) orbitals.

RPA problem, which for linear response is equivalent to the time-dependent Hartree–Fock (TDHF), is considered to be much more difficult than the underlying static HF problem, because the size of the matrix (1) is much larger than the size of the corresponding Fock matrix. Indeed, in contrast to the HF, where the number of equations scales linearly with the number of particles, the size $2N$ of the matrix (1) grows quadratically with the size of the single-particle Hilbert space. This rules out diagonalization of the matrix (1) for relatively large systems.

For small systems, the non-Hermitian eigenvalue problem can be transformed into the Hermitian eigenvalue problem for the matrix $(A+B)^{1/2}(A-B)(A+B)^{1/2}$ [18]. However, the

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0953-4075/01/120401+07$30.00

operation of taking the square root of a matrix requires its full diagonalization. In reality, a full RPA solution is often prohibitive, since the size of the RPA matrix is large. For example, the valence shell of the C_{60} molecule consists of 240 electrons that occupy 240 spin-degenerate molecular orbitals. The solution of HF equations requires diagonalization of a Hermitian Fock matrix of size 240×240. In contrast, the RPA matrix (1) in this case has dimensions $28\,800 \times 28\,800$.

On the other hand, full solution of RPA equations is not always necessary, since in many cases only a few low-energy excitonic states are of interest. Thus, the problem is to find only a few *extremal* eigenvalues and eigenvectors of the matrix (1)—a task similar to a standard problem in quantum mechanics.

In quantum mechanics extremal eigenvalues of a Hermitian matrix H are determined by the Rayleigh–Ritz minimum principle,

$$\epsilon_{\min} = \min_{(\psi\psi)=1} (\psi H \psi) \tag{2}$$

where the minimum is taken over all vectors ψ normalized as $(\psi\psi) = 1$. When the set of ψ is restricted to a certain subspace $\mathcal{K}$, equation (2) yields a variational approximation to $\epsilon_{\min}$. When $\mathcal{K}$ is chosen to be a Krylov subspace of the matrix H this procedure is equivalent to the famous Lanczos method [19, 20].

Unfortunately, no general minimum principle exists for eigenvalues of non-Hermitian matrices [21]. In addition, non-Hermitian matrices may have complex eigenvalues or may not be diagonalizable at all.

It has been greatly overlooked that, although the RPA-type matrix is non-Hermitian, its block paired structure gives it some properties similar to the Hermitian matrices. For example, when the matrices $A \pm B$ are both positive definite, the spectrum of (1) consists of N real pairs $\pm\omega$ [31].

The paired structure of (1) can be exploited to transform RPA equations into the form of Hamiltonian equations of motion for classical oscillations. Substituting $T = A + B$ and $K = A - B$ we get

$$Tp = \omega q, \qquad Kq = \omega p. \tag{3}$$

The vectors q and p play the role of the conjugate canonical coordinates and momenta, while K and T are the matrices of stiffness and kinetic coefficients respectively. Equations (3) describe the motion of a classical Harmonic oscillator near a stationary point. Thus, the lowest excitation energy of a quantum system corresponds to the lowest frequency of oscillations of an effective classical Hamiltonian oscillator near the equilibrium. This observation allows us to apply all the machinery of the classical Hamiltonian dynamics to the RPA problem.

The lowest frequency of a harmonic Hamiltonian system equals the minimum of its total energy over all phase-space configurations $\{p, q\}$ normalized by $(pq) = 1$:

$$\omega_{\min} = \min_{(pq)=1} \frac{(pTp)}{2} + \frac{(qKq)}{2}. \tag{4}$$

Indeed, variation of (4) with respect to p and q yields Hamiltonian equations of motion (3). The two terms in the right-hand side are simply the kinetic and the potential energy of the Harmonic oscillator with coordinates q and momenta p.

From the mathematical point of view, the minimum principle (4) can be viewed as a generalization of the Rayleigh minimum principle (2) to the class of non-Hermitian RPA-type eigenvalue problems. In a formal limit $T = K$, the problem becomes Hermitian, the minimum is achieved at $p = q$, and equation (4) transforms into equation (2).

From the physical point of view, equation (4) constitutes a surprising result: the lowest excitation energy of a quantum system, which is the *difference of its total energies* in the excited and ground states in turn equals (within the RPA) the minimum of an effective classical energy functional.

The stationary point of the oscillator is stable when T and K are positive definite, which in turn makes all eigenfrequencies real. Equation (4) always gives positive ω_{min}, since both terms in the right-hand side are positive at any p and q. This makes transparent the result of Chi's theorem [31].

In fact, the variational principle for RPA problems has been known for a long time. It was suggested by Thouless back in 1961 and reads [3]

$$\omega_{\mathrm{min}} = \min_{\{x,y\}} \frac{(x,y)\begin{pmatrix} A & B \\ B & A \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}}{|(xx)-(yy)|}. \tag{5}$$

The minimum is to be taken over all N-vectors x and y. The minimum always exists, since the HF stability condition keeps the numerator positive [3]. Note that the denominator can be arbitrarily small, and therefore the expression has no maximum. The minimum principle (4) is equivalent to the Thouless minimum principle (5).

The HF stability condition is usually expressed as the positive definiteness of the $2N \times 2N$ block matrix in the mumerator of equation (5). In this case the stationary point of the HF energy functional is stable, i.e. it corresponds to a true (global or local) minimum. The HF stability condition is apparently equivalent to the condition for the stationary point of the effective classical oscillator to be stable.

The minimum principle (4) can be used as a basis for building the *variationally stable* Lanczos method, in complete analogy with the Hermitian case [20, 32]. It is straightforward to verify that the following recursion:

$$q_{i+1} = \beta_{i+1}^{-1}(Tp_i - \alpha_i q_i - \beta_i q_{i-1}) \tag{6a}$$

$$p_{i+1} = \delta_{i+1}^{-1}(Kq_i - \gamma_i p_i - \delta_i p_{i-1}) \tag{6b}$$

generates configuration space vectors (q_i, p_i) that span the Krylov subspace of the eigenvalue problem (3). When four coefficients α_i, β_i, γ_i, and δ_i are chosen at each step i to ensure $(q_{i+1}p_i) = (q_{i+1}p_{i-1}) = (p_{i+1}q_i) = (p_{i+1}q_{i-1}) = 0$, the vectors p_i, q_i form a biorthogonal basis, $(p_i q_j) = \delta_{ij}$, and the matrices $\tilde{K}_{ij} = (q_i K q_j)$ and $\tilde{T}_{ij} = (p_i T p_j)$ are symmetric tridiagonal, with the only nonzero matrix elements $\tilde{T}_{ii} = \alpha_i$, $\tilde{T}_{i,i-1} = \tilde{T}_{i-1,i} = \beta_i$, $\tilde{K}_{ii} = \gamma_i$, and $\tilde{K}_{i,i-1} = \tilde{K}_{i-1,i} = \delta_i$. Expanding $q = \sum c_i q_i$ and $p = \sum d_i p_i$, we arrive at the $2n \times 2n$ eigenvalue problem

$$\tilde{T}d = \tilde{\omega}c, \qquad \tilde{K}c = \tilde{\omega}d \tag{7}$$

which has the same structure as (3). It is the direct analogue of the Rayleigh–Ritz eigenvalue problem in the Hermitian Lanczos method [20]. The lowest positive eigenvalue $\tilde{\omega}_{\mathrm{min}}$ of (7) gives the approximation to the true lowest frequency ω_{min}.

When the lowest-frequency normal mode $q^{(1)}$, $p^{(1)}$ is found, the second-lowest normal mode $q^{(2)}$, $p^{(2)}$ can be obtained by choosing initial vectors q_1 and p_1 orthogonal to $p^{(1)}$ and $q^{(1)}$, respectively. As follows from equations (6) such a choice causes all vectors q_i and p_i to remain orthogonal to $p^{(1)}$ and $q^{(1)}$. An *oblique projection* can be used to correct for the loss of orthogonality with respect to $p^{(1)}$ and $q^{(1)}$ that may occur at large n. Namely, the necessary amounts of $q^{(1)}$ and $p^{(1)}$ should be subtracted from q_i and p_i respectively, to ensure $(q_i p^{(1)}) = (p_i q^{(1)}) = 0$. Higher-frequency RPA solutions can be found one by one in this way.

The problem of the selective computation of a few low-energy excitations in molecules and other quantum many-particle systems has attracted a great deal of effort [22–30]. The crucial

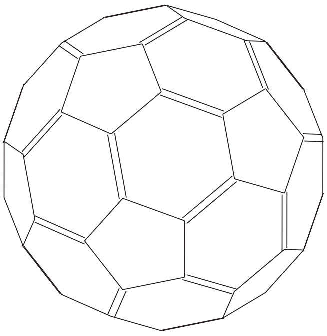

Figure 1. The geometry of C_{60} is completely determined by the single- and double-bond lengths.

new feature of the present approach is the minimum principle equation (4) that brings it the stability of a variational procedure. The variational character assures that the approximation $\tilde{\omega}_{\mathrm{min}}$ is always greater than the exact value. On the other hand, due to the same variational character, $\tilde{\omega}_{\mathrm{min}}$ decreases monotonously with increasing size n of the Krylov subspace. The accuracy is found to improve exponentially with n, in direct analogy with the Hermitian Lanczos technique.

In order to demonstrate the computational power of the method I apply it to obtain the singlet excitation spectrum of the fullerene C_{60} molecule. Even with the great amount of attention this molecule has received in the past few years [33], the calculations of the excited states of C_{60} reported so far are limited [24, 34–36]. On the other hand, the first-principle semiempirical calculation of the RPA spectrum of C_{60} is a very modest example for the power of the new technique.

The Hamiltonian matrix elements depend on the geometry of the molecule, which in turn is completely determined by the single- and double-bond lengths (see figure 1), chosen to have experimental values of 1.46 and 1.455 Å [33] respectively. The matrix elements were computed using the INDO/S approximation [37, 38], designed to yield a good description of the excitation spectra of π-conjugated molecules within the RPA [7–10].

The new technique has allowed one to easily solve RPA equations in the entire valence space of the molecule. Figure 2 shows the complete excitation spectrum obtained. A total of 600 singlet excited states have been computed sequentially using equations (6) and (7). The technique was found to deliver RPA excited states at an expense comparable to solving the static HF equations for the ground state[2].

Table 1 provides a comparison of the results to the available experimental data. The energies of the optically allowed transitions obtained match the positions of the features observed in the linear absorption of C_{60} to within a few percent [39]. The high symmetry of the molecule causes the majority of states to be optically dark. Only the states of T_{1u} symmetry have nonzero oscillator strengths and may show up in linear absorption [33]. It seems that the abundance of the singlet optically dark states in C_{60} below the first optically allowed transition has not been fully realized [33].

The problem could have been simplified by taking symmetry considerations into account

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[2] The calculation was performed on a DEC Alpha 500 au workstation. The solution to the static HF equations took about 2 min CPU time compared to about 6 min CPU time per excited state. Note that the storage capacity for the RPA matrix of size 28 800 × 28 800 would require 6.3 Gigabytes of computer memory, which at the time of calculation (November 1999) was only available on supercomputers. The generalized Lanczos recursion (6) allows one to avoid having to store the full matrix in memory, since it only requires evaluation of matrix-vector products Tp and Kq from time to time.

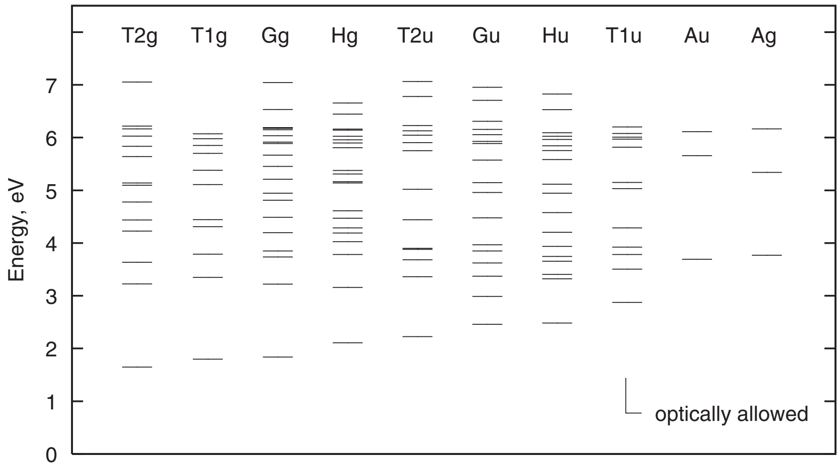

Figure 2. The low-energy part of the RPA excitation spectrum of C_{60}. Only T_{1u} states have nonzero oscillator strengths.

Table 1. Experimental and theoretical electronic excitation energies of C_{60}. Experimental values are from the linear absorption in *n*-hexane [39]. The percentage values are the deviations with respect to the experiment.

Absorption experiment [39] $\hbar\omega$ (eV)	RPA solution $\hbar\omega$ (eV)
3.04	2.874 (5%)
3.30	3.505 (6%)
3.78	3.782 (0%)
4.06	3.924 (3%)
4.35	4.287 (1%)
4.84	5.031 (4%)
5.46	5.150 (6%)
5.88	5.816 (1%)
	6.008
	6.078
6.36	6.202 (2%)

before the RPA equations are solved. It would, however, oppose the purpose of this letter, which is to demonstrate the performance of the method for a complex problem. In particular, specific difficulties could have been expected from the high level of degeneracies in the spectrum. No such difficulties have been noticed.

The symmetry analysis was performed for each state computed. Excitation energies were found to be degenerate 1, 3, 4, or 5 times in accordance with the multiplicities of the irreducible representations of the I_h symmetry group.

The choice of the initial vectors was observed to play no significant role in the convergence. The results presented above were obtained using random starting vectors. The choice of the initial vector close to the solution was found to improve the convergence at several initial iterations.

For the sake of simplicity, this letter deals mainly with finite many-particle systems that do not exhibit continuous symmetry breaking. In systems where continuous symmetry can be broken, RPA equations can have zero-frequency spurious or Goldstone modes [31]. The classical mechanics analogy developed above helps to see this point clearly: when the classical system is not at the minimum of the potential surface, motion in certain directions is unstable. When the system possesses a continuous symmetry parameter, the minimum is not unique and we have a zero-frequency mode. These situations require special treatment to project such modes out [31], which is beyond the scope of this letter.

In conclusion, an analogy between the linear response equations of quantum many-body systems and classical Hamiltonian equations of motion is revealed. It is shown that the excitation frequencies, which are *differences* of energies, are given in turn by the minimum of an effective classical energy functional. A numerical technique that follows from this observation helps to solve RPA-type equations at a computational cost comparable to the HF solution for the ground state. The method assists in computing low-energy excitonic states at the level of theory which may be hard or impossible to achieve using conventional techniques.

As suggested in [17, 40], calculation of the electronic excitation energies at various nuclear configurations effectively yields the excited-state adiabatic surface, provided that the ground-state adiabatic surface is known. Thus, the ability to compute excitation energies at a computational expense comparable to the ground-state calculation provides a long-sought opportunity to perform molecular dynamics simulations of photochemical reactions, especially those that occur in large biological molecules.

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