Electron in the Field of a Molecule with an Electric Dipole Moment

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In solving the eigenvalue wave equation, we relax the usual diagonal constraint on its matrix representation by allowing it to be tridiagonal. This results in a larger representation space that incorporates an analytic solution for the noncentral electric dipole pole potential $\cos\theta/r^2$, which was believed not to belong to the class of exactly solvable potentials. Consequently, we obtain closed form solution of the time-independent Schrödinger equation for an electron in the field of a molecule treated as a point electric dipole.

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Introduction.—The electron binding properties of polar molecules have recently been a topic of considerable theoretical [1] and experimental interest [2]. Using the Born-Oppenheimer approximation, in which the motion of the electron is calculated for fixed nuclear coordinates, it has been shown that the electric dipole field is capable of supporting an infinite number of bound states for an electron if the dipole moment is greater than a critical value equal to 1.625 D [3]. Under these circumstances, the excess electron will be bound to the molecule, giving rise to the so-called dipole-bound anion. The critical dipole moment does not depend on the size of the dipole. However, if the system is treated dynamically to include the rotational degrees of freedom of the nuclei, the infinite number of bound states becomes finite [4].

Long ago, Fermi and Teller demonstrated first that a point dipole could bind an electron in an infinite number of bound states, if its dipole strength exceeds a critical value [5]. Subsequently, several authors found that this critical dipole strength was independent of the dipole length and the presence of any short-range repulsion of the core nuclei [6]. The consideration of rotational degrees of freedom in a real molecular system reduces the number of bound states to a finite number and increases the minimum dipole strength to support at least one bound state by 10% with respect to that of a fixed dipole. In this case, the critical dipole moment depends on the dipole length, the rotational state, and the moments of inertia of the polar molecules. It is also expected that any angular momentum about the symmetry axis can only increase the energy and hence the value of the critical dipole moment [7]. From an experimental point of view, the formation of a dipole-bound anion has been difficult to observe because the much diffused and loosely bound electrons are easily stripped away by thermal collisions and/or by the electric fields to which they are exposed. However, recent experimental advances have made it possible to measure the energy of one dipole-bound electron very accurately [2].

In this Letter, we address the issue of analyticity and exactness of the solution of this problem. As a result, we do confirm the outstanding difficulty that the energy eigenvalue equation for this problem in the diagonal representation, $H|\phi_n\rangle = E_n|\phi_n\rangle$, does not have a closed form solution. This is because the noncentral electric dipole potential, $V(r,\theta) = \cos\theta/r^2$ (in spherical coordinates), is known not to belong to any of the established classes of exactly solvable potentials. However, our approach follows another path where we employ the tridiagonalization tools inspired by the J-matrix method [8]. In this program, we only require that the matrix representation of the wave operator (both radial and angular) be tridiagonal and symmetric. Therefore, the matrix wave equation results in a three-term recursion relation for the expansion coefficients of the wave function. Consequently, the problem translates into finding solutions of this recursion relation. The major contribution of our present work is that by relaxing the usual constraint on the matrix representation of the wave operator from being diagonal to allow for a tridiagonal representation, we were able to obtain an analytic solution for the electric dipole potential. Therefore, this noncentral potential becomes a new member in the class of exactly solvable potentials.

The three-dimensional time-independent Schrödinger equation for a particle of mass M and charge q in an electrostatic potential $V(\vec{r})$ is

$$\left[-\frac{\hbar^2}{2M}\vec{\nabla}^2 + qV(\vec{r}) - E\right]\psi = 0, \tag{1}$$

where the energy E is either discrete or continuous. In spherical coordinates, this wave equation is separable for potentials of the form [9].

$$V(\vec{r}) = V_r(r) + \frac{1}{r^2}\left[V_\theta(x) + \frac{1}{1-x^2}V_\phi(\phi)\right], \tag{2}$$

where $x = \cos\theta$. Thus, if we write the wave function as $\psi(r,\theta,\phi) = r^{-1}R(r)\Theta(\theta)\Phi(\phi)$, then Eq. (1) becomes separated in all three coordinates as follows

$$\left(\frac{d^2}{d\phi^2}-2V_\phi+2E_\phi\right)\Phi=0, \tag{3a}$$

$$\left[(1-x^2)\frac{d^2}{dx^2}-2x\frac{d}{dx}-\frac{2E_\phi}{1-x^2}-2V_\theta+2E_\theta\right]\Theta=0, \tag{3b}$$

$$\left(\frac{d^2}{dr^2}-\frac{2E_\theta}{r^2}-2V_r+2E\right)R=0, \tag{3c}$$

where the separation constants E_ϕ and E_θ are real and dimensionless, and we have used the atomic units $\hbar = M = q = 1$.

Now we specialize to the case where an electron is interacting with a neutral molecule that has a permanent electric dipole moment. This problem is modeled by a charged particle moving under the influence of a point electric dipole fixed at the origin with moment p pointing along the positive z axis. Thus, $V_\phi = 0$, $V_\theta = -p\cos\theta$, and $V_r = 0$, where length is measured in units of $a_0 = 4\pi\varepsilon_0\hbar^2/Mq^2$. With $V_r = 0$, Eq. (3c) becomes the wave equation for the inverse square potential. It has been well established that bound state solutions for this potential could be supported only if the dimensionless coupling parameter $2E_\theta$ is less than the critical value $-\frac{1}{4}$ [10]. Therefore, for bound states we take $2E_\theta = -\omega^2 - \frac{1}{4}$, whereas for scattering states we write $2E_\theta \equiv \gamma(\gamma+1) = (\gamma+\frac{1}{2})^2 - \frac{1}{4}$, where γ and ω are real dimensionless parameters. In the following, we obtain the angular and radial components of the wave function for both cases. These will be written as a series in terms of special functions that are compatible with the domain of the Hamiltonian and support a tridiagonal matrix representation for the wave operator.

The angular wave function.—It is straightforward to obtain the normalized solution of Eq. (3a) with $V_\phi = 0$ that satisfies the boundary conditions as $\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{\pm im\phi}$, where $m = 0, 1, 2, \ldots$, giving $E_\phi = \frac{1}{2}m^2$. Now, we expand the angular component $\Theta(\theta)$ in a complete basis set $\{\chi_n(x)\}_{n=0}^{\infty}$ as $\Theta(\theta) = \sum_{n=0}^{\infty} f_n^m(E_\theta)\chi_n(x)$. The basis elements are written as $\chi_n(x) = a_n(1-x)^\alpha \times (1+x)^\beta P_n^{(\mu,\nu)}(x)$, where $P_n^{(\mu,\nu)}(x)$ is the Jacobi polynomial of degree $n = 0, 1, 2, \ldots$. The dimensionless real parameters α, $\beta \geq 0$, μ, $\nu > -1$ and a_n is a normalization constant. The recurrence relation and orthogonality formula of the Jacobi polynomials [11] show that a tridiagonal matrix representation for $\langle\chi_n|H_\theta - E_\theta|\chi_{n'}\rangle$ is achievable with $V_\theta \sim x$ if and only if $\mu = \nu = m$ and $\alpha = \beta = \frac{1}{2}m$. As a result, we obtain the following tridiagonal structure:

$$2\langle\chi_n|H_\theta - E_\theta|\chi_{n'}\rangle = \left[\left(n+m+\frac{1}{2}\right)^2 - \left(\gamma+\frac{1}{2}\right)^2\right]\delta_{n,n'} - p\sqrt{\frac{n(n+2m)}{(n+m)^2-1/4}}\,\delta_{n,n'+1} - p\sqrt{\frac{(n+1)(n+2m+1)}{(n+m+1)^2-1/4}}\,\delta_{n,n'-1}, \tag{4}$$

where we took $2E_\theta \equiv \gamma(\gamma+1)$ for scattering solutions. Equation (3c) shows that γ plays the role of the angular momentum ℓ in central potential problems. However, unlike ℓ that assumes integral values, γ is a continuous parameter. For positive E_θ, γ must be either greater than zero or less than -1.

The tridiagonal matrix representation (4) makes the angular wave Eq. (3b) equivalent to the following recursion relation for the expansion coefficients of $\Theta(\theta)$

$$\left(\gamma+\frac{1}{2}\right)^2 H_n^m = \left(n+m+\frac{1}{2}\right)^2 H_n^m - p\frac{n+m}{n+m+1/2}H_{n-1}^m - p\frac{(n+1)(n+2m+1)}{(n+m+1/2)(n+m+1)}H_{n+1}^m, \tag{5}$$

where H_n^m are related to f_n^m through

$$f_n^m(E_\theta) = \frac{\sqrt{n+m+1/2}}{2^m\Gamma(n+m+1)} \times \sqrt{\Gamma(n+1)\Gamma(n+2m+1)}\,H_n^m(p;\gamma). \tag{6}$$

Relation (5) implies that if p is too large then the reality of the representation will be violated. Therefore, the dipole moment should not exceed a certain critical value that depends on m. Below, we show how to calculate these critical values, denoted by p_m. The solutions of the above recursion relation (for fixed p and m) are functions in γ that are defined modulo an arbitrary nonsingular factor that depends on γ but otherwise independent of n. We choose the standard normalization $H_0^m = 1$ making H_n^m a polynomial of degree n in $(\gamma+\frac{1}{2})^2$. These polynomials were not investigated previously. Since they are associated with the electric dipole potential $p\frac{\cos\theta}{r^2}$ we refer to them as the "*dipole polynomials*." For a given m and p, the recursion relation (5) together with the initial value $H_0^m = 1$ and the definition $H_{-1}^m \equiv 0$ determine the set of all polynomials $\{H_n^m(p;\gamma)\}$ completely. Now, the angular component of the wave function $\psi(r,\theta,\phi) = r^{-1}R(r)\Omega(\theta,\phi)$ could then be written as the L^2 series

$$\Omega(\theta,\phi) = A_m^{p,\gamma}e^{\pm im\phi}(1-x^2)^{m/2} \times \sum_{n=0}^{\infty}\frac{(n+m+1/2)\Gamma(n+2m+1)}{2^{2m}\Gamma(n+m+1)^2/\Gamma(n+1)} \times H_n^m(p;\gamma)P_n^{(m,m)}(x), \tag{7}$$

where m assumes any integral value such that $p_m \geq p$. $A_m^{p,\gamma}$ is a normalization constant that depends on the physical parameters of the problem. It should be obvious from Eq. (4) that the discrete diagonal representation, where $H_\theta|\chi_n\rangle = E_\theta|\chi_n\rangle$, is obtained only if $p = 0$ and

$$\gamma = \begin{cases} \ell & ;\gamma \geq 0 \\ -\ell - 1 & ;\gamma \leq -1 \end{cases},$$

where $\ell = n + m = 0, 1, 2, \ldots$. This means that a diagonal representation is obtained only in the absence of the electric dipole. This might be the reason behind the curious absence of an exact *analytic* solution to this problem in the literature.

For bound states we take $2E_\theta = -\omega^2 - \frac{1}{4}$. This is equivalent to the above with $\gamma \to i\omega - \frac{1}{2}$. Thus, the angular component of the wave function is identical to (7) but with $H_n^m(p;\gamma)$ replaced by $G_n^m(p;\omega) = H_n^m(p; i\omega - \frac{1}{2})$ and m is restricted to be less than or equal to an upper bound such that $p_m \le p$. Now, it has already been established that for the electron-dipole problem the dipole moment p must exceed a certain critical value so that the solution space for bound states becomes nonempty [1]. To obtain this critical value, we investigate Eq. (5) for f_n^m and with $\gamma \to i\omega - \frac{1}{2}$, which could now be written as the eigenvalue equation $h|f\rangle = \omega^2|f\rangle$, where h is the tridiagonal symmetric matrix

$$h_{nm} = -\left(n + m + \frac{1}{2}\right)^2 \delta_{nm} + p\sqrt{\frac{n(n+2m)}{(n+m)^2 - 1/4}}\,\delta_{n,m+1} + p\sqrt{\frac{(n+1)(n+2m+1)}{(n+m+1)^2 - 1/4}}\,\delta_{n,m-1}. \tag{8}$$

Therefore, the determinant of the matrix $h - \omega^2 I$ must vanish, where I is the identity matrix. This translates into a condition on the electric dipole moment p that depends on m and ω. The critical value p_m is the smallest value that satisfies this condition for $\omega = 0$. For the lowest few quantum numbers m, Table I shows a sequence of these critical values for an N-dimensional matrix h with $N = 2, 3, \ldots, 12$. It is evident that the sequence converges rapidly with N for the given choice of significant digits. In fact, for each N one finds a set of $2K$ zeros, $\{\pm p_i\}_{i=1}^K$, of the determinant where $K = \frac{N}{2}$ or $K = \frac{N-1}{2}$ if N is even or odd, respectively. For large N, the smallest positive zero is the critical value of the dipole moment. Table II lists the lowest few zeros for several values of the azimuthal number m. These values agree with those already obtained in [7].

The radial wave function.—It is taken as an element in the space spanned by the basis functions $\phi_k(y) = b_k y^\tau e^{-y/2} L_k^\sigma(y)$, where $k = 0, 1, 2, \ldots$, $y = \lambda r$ and $L_k^\sigma(y)$ is the Laguerre polynomial. The length scale parameter λ is positive, $\tau > 0$, $\sigma > -1$ and the normalization constant is $b_k = \sqrt{\frac{\lambda\Gamma(k+1)}{\Gamma(k+\sigma+1)}}$. We start with the scattering solution where $2E_\theta \equiv \gamma(\gamma+1)$. The recurrence relation and orthogonality formula for the Laguerre polynomials show that a tridiagonal matrix representation for $\langle\phi_k|H_r - E|\phi_{k'}\rangle$ is possible if and only if $\sigma = 2\tau - 1$ and

$$\tau = \begin{cases} \gamma + 1 & ;\gamma \ge 0 \\ -\gamma & ;\gamma \le -1 \end{cases}.$$

This makes $\tau \ge 1$ and gives $\sigma = \pm(2\gamma+1)$ for $\pm\gamma > 0$. Moreover, we obtain the following matrix elements of the radial wave operator

$$\langle\phi_k|H_r - E|\phi_{k'}\rangle = (2k+\sigma+1)\left(\frac{\lambda^2}{8} - E\right)\delta_{k,k'} + \left(\frac{\lambda^2}{8} + E\right) \times \left[\sqrt{k(k+\sigma)}\,\delta_{k,k'+1} + \sqrt{(k+1)(k+\sigma+1)}\,\delta_{k,k'-1}\right]. \tag{9}$$

Expanding $R(r)$ in the basis as $\sum_{k=0}^\infty g_k^\gamma(E)\phi_k(y)$ and using (9) in the matrix representation of the wave Eq. (3c) leads to the following recursion relation

$$2\left(k + \frac{\sigma+1}{2}\right)\cos\varphi S_k^\gamma = (k+\sigma)S_{k-1}^\gamma + (k+1)S_{k+1}^\gamma, \tag{10}$$

where $g_k^\gamma(E) = b_k S_k^\gamma(E)$ and $\cos\varphi = \frac{8E-\lambda^2}{8E+\lambda^2}$ for $E \ge 0$. This recursion relation is identical to that of the ultraspherical (Gegenbauer) polynomial $C_k^{(\sigma+1)/2}(\cos\varphi)$. Therefore, the continuum radial wave function becomes

$$R(r) = B_\gamma^E(\lambda r)^{(\sigma+1)/2} e^{-\lambda r/2} \sum_{k=0}^\infty \frac{\Gamma(k+1)}{\Gamma(k+\sigma+1)} \times C_k^{(\sigma+1)/2}(\cos\varphi) L_k^\sigma(\lambda r). \tag{11}$$

The normalization constant B_γ^E depends on γ and the energy but, otherwise, independent of k.

On the other hand, for bound states, the matrix representation of the radial wave operator, $\langle\phi_k|H_r - E|\phi_{k'}\rangle$, with $2E_\theta = -\frac{1}{4} - \omega^2$ is tridiagonal if and only if $\sigma = 2\tau - 2$ and $\lambda^2 = -8E$. The radial wave equation becomes

TABLE I. Calculated values of the dipole moment parameter (in atomic units) converging to the critical value p_m as the dimension N of the matrix representation of the angular wave operator increases.

N	$m = 0$	$m = 1$	$m=2$
2	0.649 491 141 019 818	4.220 288 503 393 705	11.804 934 601 571 14
3	0.639 369 160 661029	3.811 775 932 688 927	9.755 522 988 492 659
4	0.639 314 968 595 286	3.792 439 635 980 491	9.544 808 359 632 656
5	0.639 314 877 261 703	3.791 973 278 623 325	9.529 634 749 795 701
6	0.639 314 877 200 001	3.791 967 959 126 813	9.529 040 785 868 604
7	0.639 314 877 199 981	3.791 967 926 881 534	9.529 027 518 799 769
8	0.639 314 877 199 981	3.791 967 926 767 706	9.529 027 336 215 217
9	0.639 314 877 199981	3.791 967 926 767 456	9.529 027 334 574 952
10	0.639 314 877 199 981	3.791 967 926 767 455	9.529 027 334 564 905
11	0.639 314 877 199 981	3.791 967 926 767 455	9.529 027 334 564 862
12	0.639 314 877 199 981	3.791 967 926 767 455	9.529 027 334 564 860

TABLE II. Absolute values of the zeros (in atomic units) of the determinant of the matrix representation of the angular wave operator Eq. (8) for $N = 50$. The smallest zeros are the critical value given in Table I.

$m = 0$	$m = 1$	$m = 2$
0.639 314 877 199 981	3.791 967 926 767 455	9.529 027 334 564 860
7.546 955 713 288 350	14.112 114 595 025 52	23.398 535 107 107 28
21.300 903 309 406 47	31.301 697 888 810 59	44.066 259 541 146 74
41.927 307 152 002 01	55.365 442 853 785 35	71.586 009 323 372 22
69.428 385 700 065 42	86.304 058 712 619 84	105.971 978 601 265 0

equivalent to the following three-term recursion relation for the expansion coefficients

$$\omega^2 S_k = \left[(k+\sigma+1)\left(k+\frac{\sigma}{2}+1\right)+k\left(k+\frac{\sigma}{2}\right) - \left(\frac{\sigma+1}{2}\right)^2\right]S_k - k\left(k+\frac{\sigma}{2}\right)S_{k-1} - (k+\sigma+1)\left(k+\frac{\sigma}{2}+1\right)S_{k+1}, \tag{12}$$

where $g_k^\omega(E) = b_k S_k(\omega, E)$. One should observe the curious absence of the energy from this recursion relation. This implies that the wave equation, in this representation, is satisfied independently of any value of the energy as long as it is nonpositive (due to $\lambda^2 = -8E$). This property has a dramatic implication on the bound states energy spectrum. It implies that for any choice of negative energy a bound state could be supported. However, the diagonalization constraint on the matrix representation of the radial wave operator dictates that $E = 0$. These observations have already been reported in the literature for the inverse square potential [10]. Regularization procedures [10] and self-adjoint extensions of the Hamiltonian [12] were introduced to handle these irregularities. Now, Eq. (12) is a special case of the three-term recursion relation of the continuous dual Hahn orthogonal polynomials, $Q_k^\mu(\omega;\mu,\frac{1}{2}) = {}_3F_2\left({-k,\mu+i\omega,\mu-i\omega \atop 2\mu,\mu+1/2}\middle|1\right)$, where $\mu = \frac{\sigma+1}{2}$ [13]. Thus, we can finally write the radial component of the wave function for the bound state at energy E as

$$R(E,r) = B_\omega^E (2\eta r)^{(\sigma/2)+1} e^{-\eta r} \sum_{k=0}^{\infty} \frac{\Gamma(k+1)}{\Gamma(k+\sigma+1)} \times Q_k^{(\sigma+1)/2}\left(\omega;\frac{\sigma+1}{2},\frac{1}{2}\right) L_k^\sigma(2\eta r), \tag{13}$$

where the energy-dependent wave number η is defined by $E = -\frac{1}{2}\eta^2$.

Conclusion.—In the context of the tridiagonal representation of the single particle Hamiltonian associated with an excess electron interacting with a frozen dipolar molecule, we were able to obtain a closed form solution. The problem was reduced to finding solutions of the resulting three-term recursion relation for the expansion coefficients of the wave function in a suitable square integrable basis. The recursion relation for the angular wave function generated polynomials that were not studied in the past. We refer to them as the "*dipole polynomials*." The radial component of the wave function was also obtained analytically for the scattering as well as bound states. Therefore, the noncentral electric dipole potential $\cos\theta/r^2$ becomes a new element in the class of exactly solvable potentials.

The calculation we have performed supports the existence of a dipole-bound anion for dipole moments higher than a certain critical value. This value occurs when the ground state energy approaches zero. Critical dipole moments were evaluated not only for the ground state, where they agree with already known and experimentally verified results, but also for excited states as well. Unfortunately, there are no experimental data available for the excited states and no comparison could be made with our numerical results.

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